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Featured Article

Ene−Yne Metathesis of Allylphosphonates and Allylphosphates: Synthesis of Phosphorus-Containing 1,3-Dienes

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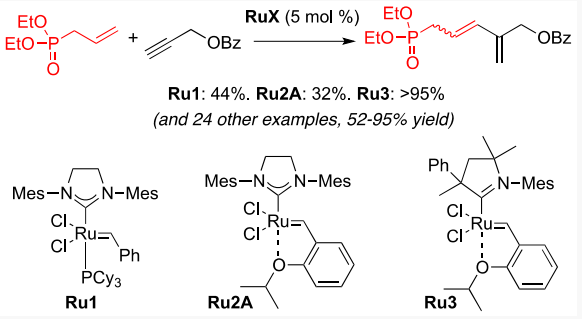
ABSTRACT: A variety of ene−yne cross metathesis reactions were performed using unsaturated phosphonate and phosphate reagents, affording the corresponding phosphorylated 1,3-diene products in good to excellent yields. These difficult ene−yne metatheses employed a Grubbs catalyst bearing a cyclic amino alkyl carbene ligand. A variety of terminal alkynes of varying substitution underwent the reaction, and different phosphorus-containing alkenes were found to give the conjugated diene products in high yields. The resulting dienes were further transformed by Horner-type Wittig reactions and a Diels−Alder cycloaddition.

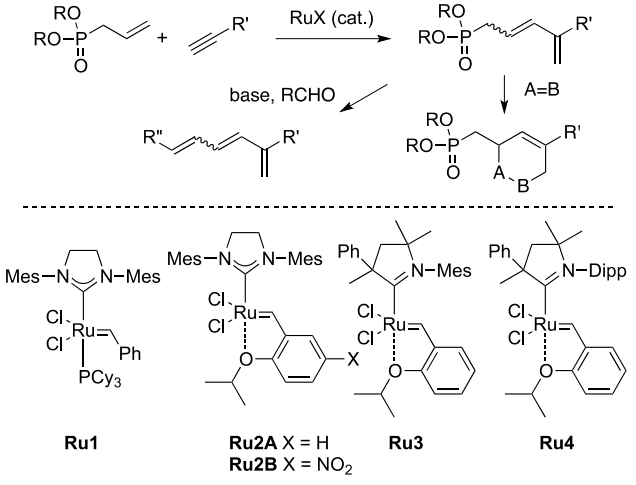


INTRODUCTION

Organophosphorus compounds are useful reagents in organic synthesis and comprise a privileged class of compounds that have numerous applications in industry as agrochemicals, fire retardants and medicines. In catalysis, phosphines R_3P are widely used as ligands, coveted because of their ability to fine tune a metal's performance in catalysis. Phosphorus-stabilized carbanions such as those used in the Horner−Wadsworth−Emmons olefination[1−4] are not only classical reagents for alkene bond synthesis but also widely used for stereoselective alkene synthesis in complex molecule total synthesis.

1,3-Dienes are versatile building blocks, but unsaturated phosphorus(V) compounds were perceived to be difficult substrates for metathesis chemistry due to their potential to coordinate through the P═O bond. This might be especially disruptive to intermolecular reactions, especially in ene−yne metathesis where alkyne concentrations must be low to avoid oligomerization side reactions.[5] There are many traditional methods for 1,3-diene functionalization, like the Diels−Alder reaction, and diverse metal-catalyzed reactions have emerged that can functionalize the ends of the diene with various heteroatoms. However, there are a limited number of examples of allylphosphonate reagents undergoing intermolecular (cross) alkene metathesis[6−9] and no examples of these reagents giving cross ene−yne metathesis. Early examples by Hanson and co-workers used unsaturated phosphonates and related compounds to construct P-heterocycles by ring-closing metathesis (RCM)[10−13] and later developed this procedure to synthesize alkenes in complex molecule synthesis.[14,15] Governeur,[16] van Boom,[17] and Schmidt[18] also made P-heterocycles by RCM or ring-closing EYM, respectively. Some of the Grubbs catalysts used for alkene and ene−yne metathesis are shown in Scheme 1 below. The second-generation Grubbs catalyst **Ru1** and the Hoveyda−Grubbs catalysts **Ru2** are typically used for most challenging applications. Hoveyda's related chiral molybdenum catalysts have been used for asymmetric RCM to construct P-heterocycles.[19] Pietrusiewicz and Grela employed vinyl

Scheme 1. Desired Cross Ene−Yne Metathesis to Provide Dienylphosphonates



Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl.

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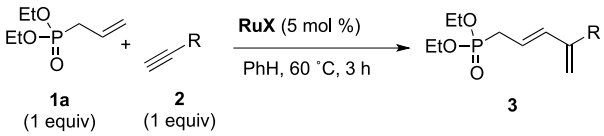
phosphine oxides in cross metathesis using the more active Grela catalyst **Ru2B**.[20] Bowen et al. dimerized diethyl allylphosphonate with **Ru1**.[21] More recently, Spilling and co-workers utilized substituted allylphosphonates in the cross alkene metathesis with the Grubbs complex **Ru1**.[22] Coordination of the P═O bond to the ruthenium carbene could deactivate catalytic intermediates, cause catalyst decomposition, or simply decrease the reaction rate, resulting in a synthetically impractical reaction. With low alkyne concentrations, these interactions could be particularly debilitating. Though active Grela catalysts have been used for difficult cross alkene metathesis, new catalysts have seldom been applied to problematic cross ene−yne metathesis. Recent work by Fogg has shown that CAAC-containing Ru carbene catalysts may overcome decomposition in alkene metathesis.[23] We speculated that Ru catalysts such as **Ru3** and **Ru4** bearing CAAC ligands instead of the N-heterocyclic carbene ligand (which characterizes the second generation Grubbs complex) might be useful in encouraging difficult cross ene−yne metathesis.

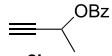
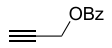
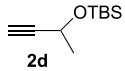
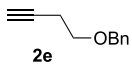
In this work, we report that unsaturated phosphorus-containing functional groups, such as allylphosphonates and homoallylphosphonates, can be joined to alkynes by ene−yne metathesis (EYM) by use of a CAAC-containing Grubbs catalyst. With this method, it is possible to access a variety of new phosphorus compounds containing the valuable 1,3-diene subunit (Scheme 1). We envisioned use of these novel products for both Wittig-type reactions and reactions of the 1,3-diene, such as Diels−Alder reactions.

RESULTS AND DISCUSSION

Initial experiments with the Grubbs catalysts gave mixed results in the cross ene−yne metathesis of allylphosphonates (Table 1). Allylphosphonate **1a** was chosen to investigate ene−yne metathesis (EYM) using various terminal alkynes. For **2a** and **2b**, excellent yields were obtained using equimolar quantities of alkene **1a** and alkyne **2** (entries 1 and 2, Table 1). Use of equimolar stoichiometry is unusual in cross EYM[24] and is highly appealing due to its atom economy.[25] However,

Table 1. Initial Studies of Allylphosphonate−Alkyne Metathesis

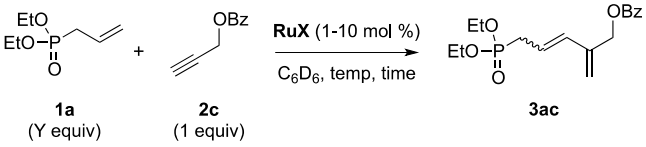


entry	alkyne	RuX	product / yield
1	 **2a**	**Ru1**	**3aa** (91%, 2:1 *E*/*Z*)
2	 **2b**	**Ru2**	**3ab** (91%, 2:1 *E*/*Z*)
3	 **2c**	**Ru1**	**3ac** (<10%, NMR)
4		**Ru2**	(<10%, NMR)
5	 **2d**	**Ru2**	**3ad** (not formed)
6	 **2e**	**Ru2**	**3ae** (not formed)

the unbranched alkyne **2c**, also possessing a benzoate group at the propargylic position, failed to react using either the Grubbs or Hoveyda−Grubbs catalysts (entries 3 and 4). Similarly, no reaction was observed for either **2d** or **2e** (entries 5 and 6). Previous mechanistic work in our group explains the poor reactivity of unbranched terminal alkynes such as **2c** and **2e**.[26] Alkyne branching was found to accelerate the slow step in the ene−yne metathesis catalytic cycle.[26,27] If there is no branching in the alkyne side chain, the overall reaction rate slows down. If this critical step in the catalytic cycle becomes too slow, decomposition may occur,[5] as we found when studying the kinetics of EYM promoted by the phosphine-free Hoveyda−Grubbs complex, **Ru2**.[27] Grubbs and Bertrand et al.[28] showed that use of Bertrand's CAAC ligand[29] in a series of novel Ru complexes resulted in a Grubbs catalyst that registered the highest turnover observed for an ethenolysis. In recent mechanistic studies, Fogg et al. found that CAAC Ru carbene catalysts can resist decomposition of ruthenacycles,[23] which can explain their increased reactivity in alkene metathesis. Lemcoff and co-workers found reduced side reactions due to isomerization when using CAAC Ru carbenes.[30] Aware of these developments and applications of CAAC Ru carbenes in challenging alkene metathesis,[28,31] we surmised that CAAC Ru carbenes might be useful for difficult cross ene−yne metathesis since some of the Ru carbene intermediates are the same. We focused our attention on the problematic coupling of phosphonate **1a** to linear alkyne **2c**.

Catalyst optimization studies determined that a CAAC-containing catalyst was superior for this ene−yne metathesis using less reactive, linear terminal alkynes (Table 2). We

Table 2. Catalyst Optimization Studies



entry	RuX (mol %)	Y	temp (°C), time (h)	yield[a] (%)
1	**Ru1** (10)	1	60, 24	<10
2	**Ru1** (10)	4	60, 3	44
3	**Ru2A** (5)	1	60, 3	<10
4	**Ru2A** (5)	1	80, 3	<10
5	**Ru2A** (5)	4	60, 3	32
6	**Ru2A** (5)	9	60, 3	71
7	**Ru3** (5)	4	60, 3	>95
8	**Ru4** (5)	4	60, 3	<10
9	**Ru3** (5)	3	60, 3	>95
10	**Ru3** (5)	2	60, 3	21
11	**Ru3** (1)	4	60, 3	<10
12	**Ru3** (5)	4	rt, 3	>95
13	**Ru3** (5)	4	rt, 1	>95
14	**Ru3** (5)	3	rt, 1	>95
15	**Ru3** (5)	2	rt, 1	25

[a]NMR yields based on integration vs mesitylene internal standard.

focused on the combination of alkene **1a** and linear (unbranched) alkyne **2c**. With a high 10 mol % catalyst loading of Grubbs' catalyst **Ru1**, increasing alkene equivalents helped but still did not give a good yield (entries 1 and 2, Table 2). The more thermally robust Hoveyda−Grubbs catalyst **Ru2A** was investigated in more detail, where low conversions were found at 60 and 80 °C, but increased yields

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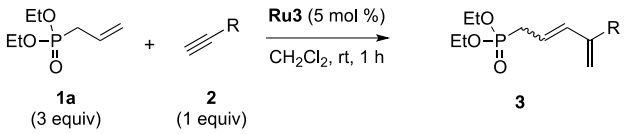
were found at 4 and 9 equiv of alkene (entries 3–6). We considered 4 equiv to be the upper limit for excess alkene because it is both wasteful and produces significantly more of the unwanted alkene homodimer. The CAAC catalysts **Ru3** and **Ru4** were next screened. The smaller **Ru3** promoted the reaction and gave greater than 95% NMR yield, but the bulkier **Ru4** gave unsatisfactory results (entries 7 and 8, respectively). Using **Ru3**, the alkene equivalents could be reduced to 3 with equal results, but the yield was found to plummet if only 2 equiv of **1a** was used (entries 9 and 10). Reduction in catalyst loading to 1 mol % was not possible (entry 11). Surprisingly, excellent reactivity was found at room temperature, and similar attempts to drop the alkene equivalents paralleled the observations at 60 °C (entries 12–15). This led us to settle on the conditions in either entry 9 or entry 14, with 3 equiv of the phosphorus reagent at either 60 °C or 25 °C.

With a suitable catalyst and lower temperature found, we investigated a variety of terminal alkynes bearing various functional groups (Table 3). Because of the lower temperatures possible with the CAAC catalyst, we elected to use dichloromethane as the reaction solvent for preparative runs. With the problematic linear alkyne **2c**, a high yield of the diene **3ac** was obtained after only 1 h in CH_2Cl_2 at rt (entry 1). The branched TBS ether worked well, providing a 68% yield of diene **3ad** (entry 2). Other linear alkynes underwent the cross metathesis to give the expected products in excellent yields (entries 3 and 4). Branching at the propargylic position of the alkyne was well tolerated (entries 5 and 6). Trimethylsilylacetylene was a good substrate and gave the product **3ai** in an unusually high 9:1 *E*/*Z* ratio (entry 7). Nitrogen functionality was tolerated (entries 8 and 9). Last, methyl propiolate **2l** underwent reaction to give the corresponding product **3al** in moderate yield, but remarkably as solely the *Z*-isomer, as evidenced by the magnitude of the coupling constant ($^3J_{HH}$ = 10.1 Hz) for the vinylic hydrogens of the 1,2-disubstituted alkene. *Z*-Selectivity is unprecedented in ene–yne metathesis, so we took a closer look at the reaction. Early aliquots showed that the reaction was not stereoselective: an initial *E*/*Z* isomeric mixture was produced; however, the *E*-isomer quickly and selectively decomposed, which upgraded the *Z*-isomer.

Next, we found that the ene–yne metathesis was general with respect to the phosphorus-containing alkene (Table 4).

Table 3. Alkyne Scope

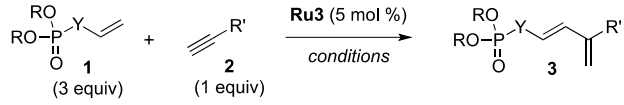


1a (3 equiv) + **2** (1 equiv) → **3**

entry	alkyne	R sidechain	1,3-diene	% yield	*E*/*Z* ratio
1	**2c**	OBz	**3ac**	77	1.5 : 1
2	**2d**	OTBS	**3ad**	68	1.5 : 1
3	**2e**	OBn	**3ae**	81	1.5 : 1
4[a]	**2f**	OTBS, OAc	**3af**	88	2 : 1
5	**2g**	Ph	**3ag**	84	2 : 1
6	**2h**	OTBS, Ph	**3ah**	84	1.5 : 1
7	**2i**	TMS	**3ai**	74	9 : 1
8	**2j**	N(Ts)(Boc)	**3aj**	95	1.5 : 1
9	**2k**	N(phthalimide)	**3ak**	75	1 : 1
10	**2l**	CO_2Me	**3al**	52	*Z* only

[a]4 equiv of **1a** used.

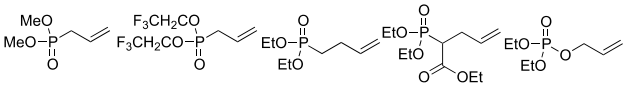
Table 4. Variation of Phosphonate Alkene Partner



1 (3 equiv) + **2** (1 equiv) → **3**

entry	alkene	Y group	alkyne	R' sidechain	1,3-diene	% yield	*E*/*Z* ratio
1[a]	**1b**	CH_2	**2f**	OTBS	**3bf**	56	1.5 : 1
2[a]	**1b**	CH_2	**2j**	NBoc(Ts)	**3bj**	80	1.2 : 1
3[b,c]	**1c**	CH_2	**2b**	OBz, OTBS	**3cb**	89	1.5 : 1
4[b]	**1c**	CH_2	**2d**	OTBS	**3cd**	74	1.2 : 1
5[b]	**1c**	CH_2	**2h**	OTBS, Ph	**3ch**	80	1.3 : 1
6[b,d]	**1d**	CH_2CH_2	**2f**	OTBS, OTBS	**3df**	70	1 : 1.2
7[b]	**1d**	CH_2CH_2	**2h**	OTBS, Ph	**3dh**	79	1 : 1
8[b]	**1e**	$CH(CO_2Et)CH_2$	**2c**	OBz	**3ec**	70	1.5 : 1
9[b,d]	**1e**	$CH(CO_2Et)CH_2$	**2f**	OTBS	**3ef**	84	1.5 : 1
10[b,d]	**1f**	OCH_2	**2f**	OTBS	**3ff**	77	2 : 1
11[b]	**1f**	OCH_2	**2h**	OTBS, Ph	**3fh**	64	2 : 1

Conditions: (a) CH_2Cl_2, rt, 1 h; (b) PhH, 60 °C, 3 h. (c) **Ru2A** used. (d) 4 equiv. alkene **1** used.



1b **1c** **1d** **1e** **1f**

We investigated two additional phosphonates bearing different esters, **1b** and **1c**; a homoallyl diethylphosphonate **1d**; an allylated *β*-ketophosphonate reagent **1e**; and allylphosphate **1f** (see bottom of Table 4). These alkene-containing reactants were subjected to intermolecular ene–yne metathesis with a variety of alkynes using the standard conditions from the table above. Dimethyl allylphosphonate gave results similar to those of the diethyl ester (entries 1 and 2, Table 4). Next, we investigated bis(trifluoroethyl)phosphonate esters, since these phosphonate reagents are valuable for stereoselective *Z*-alkene synthesis via the Still–Gennari modification[32] of the Horner–Wadsworth–Emmons (HWE) reaction. The presence of electron-withdrawing groups on the phosphonate was well tolerated but required higher reaction temperatures (entries 3–5). As expected, extending the allyl chain by one carbon did not perturb the reaction and resulted in very good yields of the expected 1,3-dienes (entries 6 and 7). Next, considering the utility of the HWE, we wanted to try an *β*-ketophosphonate **1e**, which could be used for subsequent olefination of aldehydes. Previously, we had difficulty bringing about cross ene–yne metathesis in the presence of malonates.[33] Fortunately, no difficulties were observed with this alkene, and the products were obtained in very good yields (entries 8 and 9). Finally, we examined allylphosphate as a partner. The products in entries 10 and 11 were attractive since cross coupling or substitution

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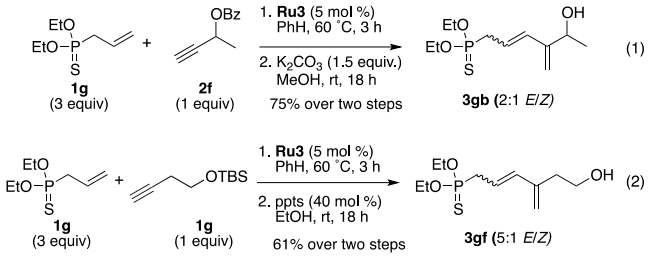
of these products would be possible, thereby extending synthetic utility of the 1,3-diene products. In the event, allylphosphate **1f** was found to be a willing partner in the cross ene−yne metathesis under the standard conditions using the CAAC catalyst **Ru3**. In all cases, the 1,3-diene products were produced as *E*/*Z* mixtures.

While not fully explored, atom economy could be achieved in some of these ene−yne metatheses. For example, in entry 3 of Table 4, 1 equiv of bis(trifluoroethyl)phosphonate **1c** was subjected to cross metathesis with 1 equiv of alkyne **2b** using catalyst **Ru2A** to give product **3cb** in 89% yield. This provides an additional example of atom economy (cf. entries 1 and 2 in Table 1).

Sulfur functionality is particularly problematic in cross metathesis since sulfur has a strong affinity for late metals such as Ru.[34−37] Since thiophosphonates are known to give higher yields in Horner−Wittig reactions,[38] we decided to investigate the compatibility of the P═S functional group with the Ru-catalyzed ene−yne metathesis. We explored the thiophosphonate **1g** under analogous conditions as given above to find excellent conversion in the ene−yne metathesis. However, in these two examples (Scheme 2), it proved difficult

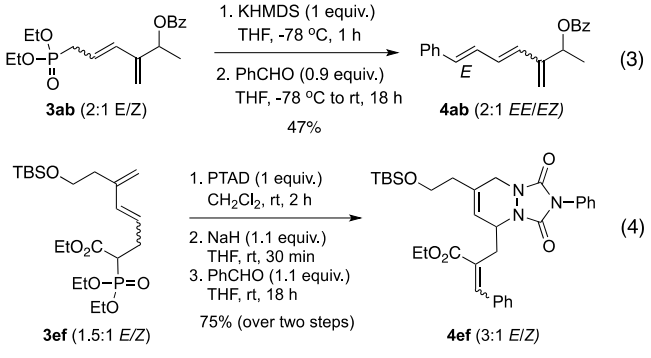
Scheme 2. Thiophosphonate Ene−Yne Metathesis and Protecting Group Removal



to separate the diene products from the unreacted alkene **1g** or its homodimer. Accordingly, either a saponification or mild desilylation was conducted to give the corresponding alcohols **3gb** and **3gf** in good isolated yields over the two steps.

Last, we found that dienyl phosphonates underwent Horner−Wittig reactions and a Diels−Alder reaction (Scheme 3). Deprotonation of dienyl phosphonate **3ab** with KHMDS and subsequent condensation with benzaldehyde provided the expected triene in good yield (eq 3). The newly formed alkene was formed as the *E*-isomer, and the 2:1 *E*/*Z* mixture of the middle double bond was the same 2:1 *E*/*Z* isomeric composition as found in the starting diene.[39] In eq 4, the

Scheme 3. Reactions of Dienyl Phosphonates



diene **3ef** underwent facile [4 + 2] cycloaddition with phenyl-1,3,4-triazol-2,5-dione (PTAD);[40−43] subsequent deprotonation and Horner−Wadsworth−Emmons reaction with benzaldehyde afforded cycloadduct **4ef** with the trisubstituted alkene in the side chain formed as a 3:1 *E*/*Z* mixture.

CONCLUSION

In conclusion, dienes can be synthesized by ene−yne metathesis between phosphorus-containing alkenes and alkynes using a suitable Grubbs catalyst bearing a cyclic alkyl amino carbene (CAAC) ligand. In the best cases, atom-economical coupling of 1 equiv of alkene and 1 equiv of alkyne could be achieved. Mostly, diethyl allylphosphonate and diethyl homoallyl phosphonate were used as alkene reactants, but other phosphorus-containing functional groups were also found to be good substrates. The superiority of a CAAC-containing Grubbs catalyst had not been demonstrated previously for ene−yne metathesis. Most likely, the superior performance of this catalyst is due to improved catalyst lifetime through analogy to alkene metathesis; however, no kinetic or mechanistic studies were done in this work. The usefulness of these catalysts may extend to other problematic metatheses; on the basis of this work, it seems prudent to consider the use of CAAC types of Ru catalysts (Bertrand−Grubbs catalysts) in cross ene−yne metathesis. Synthetic utility of the products was demonstrated through condensation of phosphorus-stabilized carbanions with aldehydes, through diene functionalization, or both.

EXPERIMENTAL SECTION

A. General Information. Unless stated otherwise, all reactions were performed in oven-dried glassware equipped with a magnetic stir bar and carried out under a nitrogen atmosphere. CH_2Cl_2, Et_2O, and THF were degassed by bubbling the solvent with argon gas and subsequently dried by passage through an activated alumina column while under an argon atmosphere via a solvent purification system. Benzene was degassed similarly and subsequently dried by passage through an activated alumina and Q5 column via a solvent purification system. All reagents used were purchased from commercial vendors and used without further purification, unless otherwise noted. Reactions carried out at −78 °C, 0 °C, and temperatures above room temperature were accomplished using a dry ice/acetone, ice/water and a mineral oil (up to 80 °C)/sand bath (>80 °C), respectively. Flash column chromatography was carried out on SiliCycle 60 Å (230−400 mesh) silica gel. TLC analysis was performed on glass-backed EM Sciences F254 silica plates and were visualized using a UV lamp and/or developed in a potassium permanganate stain.

The ruthenium carbene catalysts used were obtained from Umicore and used as received. Catalytic reactions were terminated by the addition of either ethyl vinyl ether (0.15 mL per mmol of alkyne) or a methanolic solution of potassium isocyanoacetate (KO_2CCH_2NC). Potassium isocyanoacetate was prepared and used as previously reported (0.20 equiv in methanol).[44]

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on either a 300 MHz, 400 or 500 MHz Varian spectrometer with the appropriate frequency reported. ^1H and ^{13}C NMR spectra obtained in $CDCl_3$ were internally standardized via the trace chloroform signals at 7.26 and 77.0 ppm, respectively. ^{31}P NMR spectra obtained in $CDCl_3$ were standardized by use of triphenylphosphine in $CDCl_3$ as an external reference set to −6.0 ppm. *E*/*Z* ratios were based on integrations in the ^1H spectra. Integrations for ^{31}P NMR signals were found to agree closely with the *E*/*Z* ratios determined by ^1H NMR spectroscopy; however, here we report major and minor ^{31}P resonances since the integrations are only approximate due to short relaxation delays (2 s) used.

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B. Preparation of Starting Materials. *Diethyl Allylphosphonate (**1a**).* Freshly distilled triethyl phosphite (7.95 mL, 46.4 mmol) and allyl bromide (7.80 mL, 90.1 mmol) were added to a 50 mL round bottom (rb) flask. The flask was then equipped with a reflux condenser and heated to reflux (ca. 70 °C) for 18 h with vigorous stirring. Volatile organics were then removed via rotatory evaporation, and the crude oil was then fractionally distilled (bp 86−90 °C/6 mmHg) under high vacuum to afford **1a** as a clear colorless oil (7.31 g, 89%). Spectral data obtained match literature reports.[45]

*Dimethyl Allylphosphonate (**1b**).* Compound **1b** was prepared similarly to **1a**. Freshly distilled trimethyl phosphite (5.30 mL, 44.9 mmol) and allyl bromide (7.80 mL, 90.1 mmol) were added to a 50 mL rb flask while under a nitrogen atmosphere. The flask was then equipped with a reflux condenser and heated to reflux (ca. 70 °C) for 18 h with vigorous stirring. Volatile organics were then removed via rotatory evaporation, and the crude oil was then fractionally distilled (bp 64−67 °C/6 mmHg) under high-vacuum. Initial fractions (ca. 3 mL) were liberally discarded, and distillation was stopped early prior to distilling the remaining oil (ca. 1 mL) to afford **1b** as a clear colorless oil (1.92 g, 28%). Spectral data obtained match literature reports.[46]

*Bis(2,2,2-trifluoroethyl) Allylphosphonate (**1c**).* Compound **1c** was prepared similarly to a previous report.[7] Tris(2,2,2-trifluoroethyl) phosphite (95% purity, 1.10 mL, 5.0 mmol), allyl bromide (0.89 mL, 10.3 mmol), and tetrabutylammonium iodide (93 mg, 0.25 mmol) were added to a 25 mL PTFE sealed heavy glass walled reaction vessel. The reaction mixture was then heated (ca. 140 °C) for 18 h with vigorous stirring. Volatile organics were removed via rotatory evaporation, and the crude oil was then purified by flash column chromatography on silica gel (eluent: 20% to 25% ethyl acetate in hexanes) to afford **1c** as a clear pale-yellow oil (893 mg, 63%). Analytical TLC: R_f = 0.28 (25% ethyl acetate in hexanes). Spectral data obtained matched the literature.[7]

*Diethyl But-3-enyl-1-phosphonate (**1d**).* Freshly distilled triethyl phosphite (4.25 mL, 24.6 mmol) and 4-bromo-1-butene (7.50 mL, 73.5 mmol) were added to a 50 mL round bottomed flask, which was then equipped with a reflux condenser. The reaction mixture was then heated (ca. 140 °C) to reflux for 48 h with vigorous stirring. Volatile organics were removed via rotatory evaporation, and the crude oil was then fractionally distilled (bp 106−110 °C/8 mmHg) under high vacuum to afford **1d** as a clear colorless oil (2.74 g, 58%). Spectral data obtained match literature reports.[47]

*Ethyl 2-(Diethoxyphosphoryl)pent-4-enoate (**1e**).* **1e** was prepared using a modified procedure from literature. Sodium hydride (60% dispersion in oil, 401 mg, 10.0 mmol) was added to a 50 mL round bottomed flask and suspended in THF (20 mL). Triethyl phosphonoacetate (5.00 mL, 25.0 mmol) was added dropwise, which resulted in a clear solution. The mixture was allowed to stir for 30 min at room temperature and allyl bromide (0.87 mL, 10.1 mmol) was then added. The reaction mixture was then allowed to stir overnight; A white precipitate had formed after 5 min of adding the alkyl halide. A saturated aqueous solution of NH_4Cl (10 mL) was then added and the organic layer was removed. The aqueous layer was then extracted with Et_2O (3x, 15 mL) and the organic layers were combined. The organic layer was then extracted with water (10 mL) and then brine (10 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated and purified by flash column chromatography on silica gel (eluent: 40−45% ethyl acetate in hexanes) to afford **1e** as a clear colorless oil (1.77 g, 67%). Analytical TLC: R_f = 0.21 (50% ethyl acetate in hexanes). Spectral data obtained match literature reports.[48]

*Diethyl Allylphosphate (**1f**).* Compound **1f** was prepared using a modified procedure from the literature. Anhydrous ethanol (6.10 mL, 104.5 mmol) and anhydrous triethylamine (14.50 mL, 104.0 mmol) were added to a 250 mL three-necked rb flask and were subsequently dissolved in Et_2O (ca. 1.0 M). The flask was then cooled to 0 °C and was equipped with an addition funnel, which was then charged with freshly distilled phosphoryl chloride (4.65 mL, 49.9 mmol). Phosphoryl chloride was then slowly added (ca. 1 drop every 10 s). After addition, the reaction mixture was allowed to warm to room temperature and stir overnight. The reaction mixture was then filtered through a 2 cm pad of Celite, which was then washed with Et_2O (20 mL). The filtrate was then concentrated via rotatory evaporation to afford crude diethyl chlorophosphate, which was used immediately in the next step. ^{31}P NMR of the crude product showed a 94:6 ratio of diethyl chlorophosphate/triethyl phosphate.

Allyl alcohol (2.70 mL, 39.7 mmol), triethylamine (8.50 mL, 61.0 mmol), and DMAP (1.23 g, 10.0 mmol) were added to a 250 mL three-necked rb flask and were subsequently dissolved in CH_2Cl_2 (ca. 0.25 M). The flask was then cooled to 0 °C and was equipped with an addition funnel, which was charged with the crude diethyl chlorophosphate prepared in the previous step. Crude diethyl chlorophosphate was then slowly added (ca. 1 drop every 20 s). After addition, the reaction mixture was allowed to warm to room temperature and stir overnight. The reaction mixture was then extracted with a saturated aqueous solution of sodium bicarbonate (150 mL), and the organic layer was removed. The aqueous layer was then extracted with CH_2Cl_2 (2×, 30 mL). The organic layers were then combined and extracted with water (150 mL) and then brine (150 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated via rotatory evaporation and passed through a silica plug (eluent: 50% ethyl acetate in hexanes). This afforded **1f** as a clear colorless oil (3.69 g, 48%). Spectral data obtained match literature reports.[49]

*O,O-Diethyl Allylphosphonothioate (**1g**).* Compound **1a** (902 mg, 5.06 mmol) and freshly recrystallized Lawesson's reagent (2.03 g, 5.02 mmol) were added to a 50 mL rb flask, and toluene (20 mL) was subsequently added. The flask was then equipped with a reflux condenser and heated to reflux. Solids had dissolved after 30 min of refluxing, and the reaction mixture was then allowed to stir overnight. The reaction mixture was then cooled to room temperature, and a precipitate formed upon exposure to air. The reaction mixture was then filtered through a 2 cm pad of Celite, which was then washed with toluene (2×, 20 mL). The foul smelling filtrates were then combined and carefully concentrated via rotatory evaporation under high vacuum. The crude residue was then purified by flash column chromatography on silica gel (eluent: 0−2% ethyl acetate in hexanes) to afford **1g** as a clear colorless oil with a slight rotten egg smell (614 mg, 63%). Analytical TLC: R_f = 0.45 (5% ethyl acetate in hexanes). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 5.92−5.70 (m, 1H), 5.28−5.12 (m, 2H), 4.24−3.98 (m, 4H), 2.81 (dd, $^2J_{HP}$ = 19.5 Hz, $^3J_{HH}$ = 7.3 Hz, 2H), 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 127.9 (d, $^2J_{CP}$ = 10.4 Hz), 120.3 (d, $^3J_{CP}$ = 15.3 Hz), 62.8 (d, $^2J_{CP}$ = 7.0 Hz), 40.8 (d, $^1J_{CP}$ = 109.8 Hz), 16.3 (d, $^3J_{CP}$ = 6.9 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 93.13 (s). FT-IR (neat, cm^{-1}): 2954, 2929, 2856, 2252, 1773, 1709, 1631, 1601, 1503, 1471, 1458, 1412, 1291, 1252, 1219, 1201, 1174, 1134, 1096, 1027, 1006, 974, 912, 835, 811, 775, 766, 731, 689, 663, 645, 617, 574, 506. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_7H_{15}O_2PSNa$ 217.0423, found 217.0430.

C. Optimization Procedure. Compounds **1a** (9 mg, 0.05 mmol) and **3c** (8 mg, 0.05 mmol) were added to an oven-dried 1 dram vial. A solution of **Ru1** (ca. 5.0 μM in C_6D_6, 1 mL) was added to the vial. The empty space of the vial was purged with a stream of nitrogen gas and was subsequently capped and sealed with parafilm. The vial was then heated to 60 °C and allowed to stir for 24 h. Mesitylene (2.3 μL, 0.17 mmol) was then added to the mixture and stirred for 1 min. ^1H NMR and ^{31}P NMR of the reaction mixture was then taken with a 25 s relaxation delay between scans; olefinic signals in ^1H NMR were compared to mesitylene for yield and ^{31}P NMR was qualitatively used to observe any new signals that may be representative to product/byproduct formation.

D. General Procedures for Ene−Yne Metathesis. *General Procedure A.* Compounds **1** and **2** were added to a rb flask and were subsequently dissolved in benzene (ca. 0.05−0.10 M) while under a nitrogen atmosphere. **RuX** (ca. 5 mol %) was then added, and the flask was subsequently equipped with a reflux condenser. The reaction mixture was then heated to 60 °C and allowed to stir for 3 h. The

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catalytic reaction was then terminated by the addition of ethyl vinyl ether or a methanolic solution of potassium isocyanoacetate followed by an additional 0.5 h of stirring. The reaction mixture was then concentrated via rotatory evaporation and purified by flash column chromatography on silica gel to afford **3**.

General Procedure B. Compounds **1** and **2** were added to a rb flask and were subsequently dissolved in CH_2Cl_2 (ca. 0.05 M) while under a nitrogen atmosphere. **RuX** (ca. 5 mol %) was then added, and the reaction mixture was stirred for 1−3 h at room temperature. The catalytic reaction was then terminated by the addition of ethyl vinyl ether or a methanolic solution of potassium isocyanoacetate followed by an additional 0.5 h of stirring. The reaction mixture was then concentrated via rotatory evaporation and purified by flash column chromatography on silica gel to afford **3**.

E. New Organophosphorus Compounds by Ene−Yne Cross Metathesis. *Diethyl (4-Phenylpenta-2,4-dien-1-yl)phosphonate (**3aa**).* Compounds **1a** (546 mg, 3.06 mmol), freshly distilled **2a** (314 mg, 3.07 mmol), and **Ru1** (135 mg, 0.16 mmol) were used following general procedure A (ca. 0.10 M). The catalyst was quenched with ethyl vinyl ether, which afforded **3aa** after flash chromatography on silica gel (eluent: ethyl acetate) as a dark brown oil with a 2:1 *E*/*Z* ratio (780 mg, 91%). Analytical TLC: R_f = 0.46 (100% ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.40−7.21 (m, 5H), 6.38 (dddt, $^3J_{HH}$ = 15.6 Hz, $^4J_{HP}$ = 5.1 Hz, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 0.6 Hz, 0.65H), 6.31 (dddt, $^3J_{HH}$ = 11.4 Hz, $^4J_{HP}$ = 4.3 Hz, $^4J_{HH}$ = 1.7 Hz, $^4J_{HH}$ = 1.5 Hz, 0.35H), 5.73 (ddt, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 7.0 Hz, 0.35H), 5.55 (ddt, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.65H), 5.55 (s, 0.35H), 5.28−5.25 (m, 0.35H), 5.19−5.17 (m, 0.65H), 5.10−5.07 (m, 0.65H), 4.08−3.97 (m, 4H), 2.69 (ddd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 0.75H), 2.60 (ddd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1.5H), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 147.2 (d, $^4J_{CP}$ = 4.2 Hz), 143.3 (d, $^4J_{CP}$ = 3.6 Hz), 139.8 (d, $^5J_{CP}$ = 0.6 Hz), 139.7 (d, $^5J_{CP}$ = 1.6 Hz), 136.1 (d, $^3J_{CP}$ = 14.7 Hz), 133.0 (d, $^3J_{CP}$ = 14.6 Hz), 128.2, 128.01, 127.98, 127.7, 127.4, 126.4, 122.1 (d, $^2J_{CP}$ = 12.0 Hz), 121.9 (d, $^2J_{CP}$ = 10.7 Hz), 116.1 (d, $^5J_{CP}$ = 4.1 Hz), 115.4 (d, $^2J_{CP}$ = 2.8 Hz), 61.8 (d, $^2J_{CP}$ = 6.7 Hz), 61.7 (d, $^2J_{CP}$ = 6.5 Hz), 30.7 (d, $^1J_{CP}$ = 138.7 Hz), 26.8 (d, $^1J_{CP}$ = 139.4 Hz), 16.3 (d, $^3J_{CP}$ = 5.7 Hz), 16.3 (d, $^3J_{CP}$ = 5.5 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.88 (s, minor), 26.20 (s, major). FT-IR (neat, cm^{-1}): 2982, 2938, 2908, 1738, 1726, 1494, 1443, 1390, 1369, 1054, 1032, 963, 777, 703. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{21}NaO_3PNa$ 303.1121, found 303.1117.

*(±)-6-(Diethoxyphosphoryl)-3-methylenehex-4-en-2-yl Benzoate (**3ab**).* Compounds **1a** (357 mg, 2.00 mmol), (±)-**2b** (350 mg, 2.01 mmol), and **Ru2** (64 mg, 0.10 mmol) were used following general procedure A (ca. 0.10 M). The catalyst was quenched with ethyl vinyl ether, which afforded **3ab** after flash chromatography on silica gel (eluent: ethyl acetate) as a dark brown oil with a 2:1 *E*/*Z* ratio (641 mg, 91%). Analytical TLC: R_f = 0.47 (100% ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.08−8.02 (m, 2H), 7.58−7.53 (m, 1H), 7.46−7.41 (m, 2H), 6.22−6.13 (m, 1H), 5.84 (ddt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 7.4 Hz, 0.65H), 5.80 (q, $^3J_{HH}$ = 6.6 Hz, 0.65H), 5.73 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HP}$ = 6.8 Hz, 0.35H), 5.56 (q, $^3J_{HH}$ = 6.6 Hz, 0.35H), 5.39 (s, 0.35H), 5.29 (s, 0.65H), 5.25 (s, 0.35H), 5.15 (s, 0.65H), 4.16−4.01 (m, 4H), 2.90−2.74 (m, 0.7H), 2.70 (ddt, $^3J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1.3H), 1.53 (d, $^3J_{HH}$ = 6.6 Hz, 2H), 1.45 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 1.33−1.20 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 165.74, 165.72, 145.7 (d, $^4J_{CP}$ = 3.9 Hz), 144.0 (d, $^4J_{CP}$ = 3.3 Hz), 133.7, 133.6 (d, $^3J_{CP}$ = 14.9 Hz), 133.1, 130.57, 130.55, 130.3 (d, $^3J_{CP}$ = 14.7 Hz), 129.73, 129.68, 128.47, 128.47, 122.7 (d, $^2J_{CP}$ = 10.8 Hz), 112.0 (d, $^2J_{CP}$ = 12.0 Hz), 114.9 (d, $^5J_{CP}$ = 2.9 Hz), 114.6 (d, $^5J_{CP}$ = 4.0 Hz), 73.3 (d, $^5J_{CP}$ = 2.0 Hz), 70.6, 62.2 (d, $^2J_{CP}$ = 3.3 Hz), 62.10 (d, $^2J_{CP}$ = 3.3 Hz), 62.05 (d, $^2J_{CP}$ = 1.0 Hz), 62.0 (d, $^2J_{CP}$ = 1.0 Hz), 31.3 (d, $^1J_{CP}$ = 139.7 Hz), 27.3 (d, $^1J_{CP}$ = 141.3 Hz), 20.4, 19.8, 16.6, 16.5. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.77 (s, minor), 26.10 (s, major). FT-IR (neat, cm^{-1}): 3443, 2982, 2934, 2907, 1716, 1647, 1602, 1584, 1478, 1451, 1392, 1369, 1315, 1267, 1176, 1163, 1099, 1054, 1024, 961, 867, 728, 794, 713, 688, 593, 530. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{18}H_{25}O_5PNa$ 375.1332, found 375.1339.

*5-(Diethoxyphosphoryl)-2-methylenepent-3-en-1-yl Benzoate (**3ac**).* Compounds **1a** (273 mg, 1.53 mmol), **2c** (83 mg, 0.52 mmol), and **Ru3** (16 mg, 0.026 mmol) were used following general procedure B for 1 h. The catalyst was quenched with potassium isocyanoacetate, which afforded **3ac** after flash chromatography on silica gel (eluent: 80% ethyl acetate in hexanes) as a pale-yellow oil with a 1.5:1 *E*/*Z* ratio (135 mg, 77%). Analytical TLC: R_f = 0.60 (100% ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.00−7.89 (m, 2H), 7.50−7.43 (m, 1H), 7.37−7.31 (m, 2H), 6.16 (dd, $^3J_{HH}$ = 16.0 Hz, $^4J_{HP}$ = 5.0 Hz, 0.6H), 6.02 (dd, $^3J_{HH}$ = 11.6 Hz, $^4J_{HP}$ = 4.5 Hz, 0.4H), 5.68 (ddt, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 7.7 Hz, 0.6H), 5.59 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.4H), 5.32 (s, 0.4H), 5.25 (s, 0.4H), 5.23 (s, 0.6H), 5.13 (s, 0.6H), 4.89 (s, 1.2H), 4.73 (s, 0.8H), 4.06−3.93 (m, 4H), 2.75 (dd, $^2J_{HP}$ = 22.6 Hz, $^3J_{HH}$ = 8.1 Hz, 0.8H), 2.57 (dd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 7.6 Hz, 1.2H), 1.21 (t, $^3J_{HH}$ = 7.1 Hz, 2.4H), 1.17 (t, $^3J_{HH}$ = 7.1 Hz, 3.6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 166.3, 166.2, 140.0 (d, $^4J_{CP}$ = 4.2 Hz), 139.2, 134.2 (d, $^3J_{CP}$ = 14.8 Hz), 133.20, 133.18, 130.8 (d, $^3J_{CP}$ = 14.7 Hz), 130.14, 130.13, 129.8, 129.7, 128.52, 128.50, 122.4 (d, $^2J_{CP}$ = 11.1 Hz), 120.0 (d, $^2J_{CP}$ = 11.9 Hz), 117.9 (d, $^5J_{CP}$ = 3.8 Hz), 117.2 (d, $^5J_{CP}$ = 3.0 Hz), 67.0 (d, $^5J_{CP}$ = 1.9 Hz), 64.5, 62.13 (d, $^2J_{CP}$ = 6.7 Hz), 62.09 (d, $^2J_{CP}$ = 6.8 Hz), 31.3 (d, $^1J_{CP}$ = 138.9 Hz), 27.4 (d, $^1J_{CP}$ = 140.0 Hz), 16.6, 16.5. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.50 (s, minor), 26.00 (s, major). FT-IR (neat, cm^{-1}): 3444, 2982, 2932, 2907, 1718, 1649, 1602, 1584, 1451, 1392, 1368, 1315, 1263, 1176, 1163, 1110, 961, 804, 783, 712, 688, 674, 617, 530. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{23}NaO_5PNa$ 361.1175, found 361.1181.

*Diethyl (5-((tert-Butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl)phosphonate (**3ad**).* Compounds **1a** (268 mg, 1.50 mmol), (±)-**2d** (91 mg, 0.50 mmol), and **Ru3** (16 mg, 0.025 mmol) were used following general procedure B for 1 h. The catalyst was quenched with ethyl vinyl ether, which afforded **3ad** after flash chromatography on silica gel (eluent: 40% ethyl acetate in hexanes) as a dark-brown oil with a 1.5:1 *E*/*Z* ratio (122 mg, 68%). Analytical TLC: R_f = 0.23 (50% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.10 (dd, $^3J_{HH}$ = 16.0 Hz, $^4J_{HP}$ = 5.2 Hz, 0.6H), 6.06 (ddt, $^3J_{HH}$ = 11.6 Hz, $^4J_{HP}$ = 4.1 Hz, $^4J_{HH}$ = 1.2 Hz, 0.4H), 5.70 (ddt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 7.7 Hz, 0.6H), 5.62 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 0.4H), 5.24 (s, 0.4H), 5.17 (s, 0.6H), 5.04 (s, 0.4H), 4.97 (s, 0.6H), 4.46 (q, $^3J_{HH}$ = 6.3 Hz, 0.6H), 4.20 (q, $^3J_{HH}$ = 6.3 Hz, 0.4H), 4.15−4.00 (m, 4H), 2.81−2.72 (m, 0.8H), 2.61 (dd, $^2J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 7.5 Hz, 0.8H), 1.31−1.26 (m, 6H), 1.25 (d, $^3J_{HH}$ = 6.3 Hz, 1.8H), 1.16 (d, $^3J_{HH}$ = 6.4 Hz, 1.8H), 0.86 (s, 9.0H), 0.02 (s, 1.2H), 0.02 (s, 1.8H), 0.01 (s, 1.2H), 0.01 (s, 1.8H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 150.0 (d, $^4J_{CP}$ = 2.4 Hz), 148.2 (d, $^4J_{CP}$ = 2.0 Hz), 134.2 (d, $^3J_{CP}$ = 14.9 Hz), 131.2 (d, $^3J_{CP}$ = 14.8 Hz), 121.2 (d, $^2J_{CP}$ = 10.8 Hz), 118.7 (d, $^2J_{CP}$ = 12.0 Hz), 113.0 (d, $^5J_{CP}$ = 3.8 Hz), 112.4 (d, $^5J_{CP}$ = 2.7 Hz), 71.6 (d, $^5J_{CP}$ = 1.8 Hz), 69.0, 62.04 (d, $^2J_{CP}$ = 6.7 Hz), 62.01 (d, $^2J_{CP}$ = 6.6 Hz), 61.93 (d, $^2J_{CP}$ = 6.7 Hz), 61.89 (d, $^2J_{CP}$ = 6.6 Hz), 31.3 (d, $^1J_{CP}$ = 138.9 Hz), 27.4 (d, $^1J_{CP}$ = 140.4 Hz), 25.91, 25.90, 24.8, 23.8, 18.3, 16.54 (d, $^3J_{CP}$ = 5.9 Hz), 16.52 (d, $^3J_{CP}$ = 6.0 Hz), −4.78, −4.83, −4.9, −5.0. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 27.08 (s, minor), 26.38 (s, major). FT-IR (neat, cm^{-1}): 2956, 2930, 2899, 2857, 1635, 1473, 1463, 1444, 1390, 1368, 1251, 1163, 1114, 1095, 1054, 1027, 963, 834, 814, 775, 668, 593, 526. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{35}NaO_4PSiNa$ 385.1934, found 385.1945.

*Diethyl (7-(Benzyloxy)-4-methylenehept-2-en-1-yl)phosphonate (**3ae**).* Compounds **1a** (268 mg, 1.50 mmol), **2e** (88 mg, 0.51 mmol), and **Ru3** (16 mg, 0.025 mmol) were used following general procedure B for 1 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3ae** after flash chromatography on silica gel (eluent: 80% ethyl acetate in hexanes) as a pale-yellow oil with a 1.5:1 *E*/*Z* ratio (145 mg, 81%). Analytical TLC: R_f = 0.35 (100% ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.35−7.29 (m, 4H), 7.29−7.23 (m, 1H) 6.18 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 5.0 Hz, 0.6H), 6.00 (dd, $^3J_{HH}$ = 11.5 Hz, $^4J_{HP}$ = 4.3 Hz, 0.4H), 5.65

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(ddt, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.5 Hz, 0.6H), 5.54 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 7.7 Hz, 0.7H), 5.02 (s, 0.4H), 5.02 (s, 0.4H), 5.02 (s, 0.4H), 4.95 (s, 0.6H), 4.93 (s, 0.6H), 4.49 (s, 1.2H), 4.48 (s, 0.8H), 4.41−4.02 (m, 4H), 3.48 (t, $^3J_{HH}$ = 6.4 Hz, 1.2H), 3.45 (t, $^3J_{HH}$ = 6.4 Hz, 0.8H), 2.79 (ddd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 7.9 Hz, $^2J_{HH}$ = 1.6 Hz, 0.8H), 2.63 (dd, $^2J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1.2H), 2.29 (t, $^3J_{HH}$ = 7.7 Hz, 1.2H), 2.18 (t, $^3J_{HH}$ = 7.7 Hz, 0.8H), 1.80 (tt, $^3J_{HH}$ = 7.7, 6.5 Hz, 1.2H), 1.72 (tt, $^3J_{HH}$ = 7.7, 6.4 Hz, 0.8H), 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 3.6H), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 2.4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 145.1 (d, $^4J_{CP}$ = 4.1 Hz), 144.0 (d, $^4J_{CP}$ = 3.5 Hz), 138.7, 138.6, 136.9 (d, $^3J_{CP}$ = 14.6 Hz), 134.2 (d, $^3J_{CP}$ = 14.7 Hz), 128.4, 128.4, 127.68, 127.67, 127.58, 127.56, 120.0 (d, $^2J_{CP}$ = 10.7 Hz), 118.2 (d, $^2J_{CP}$ = 12.0 Hz), 115.4 (d, $^5J_{CP}$ = 3.8 Hz), 114.5 (d, $^5J_{CP}$ = 2.7 Hz), 73.0, 73.0, 69.9, 69.7, 62.0 (d, $^2J_{CP}$ = 6.7 Hz), 61.9 (d, $^4J_{CP}$ = 6.7 Hz), 33.5 (d, $^5J_{CP}$ = 1.9 Hz), 30.9 (d, $^1J_{CP}$ = 139.7 Hz), 28.5, 28.3, 28.2, 27.2 (d, $^1J_{CP}$ = 140.8 Hz), 16.52 (d, $^3J_{CP}$ = 6.0 Hz), 16.50 (d, $^3J_{CP}$ = 6.1 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 27.06 (s, minor), 26.50 (s, major). FT-IR (neat, cm^{-1}): 2980, 2930, 2856, 2100, 1719, 1605, 1496, 1478, 1454, 1392, 1366, 1249, 1163, 1099, 1023, 961, 781, 737, 698, 606, 530. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{29}O_4PNa$ 375.1696, found 375.1694.

*Diethyl (6-((tert-Butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl)phosphonate (**3af**).* Compounds **1a** (719 mg, 4.03 mmol), **2f** (185 mg, 1.00 mmol) and **Ru3** (31 mg, 0.050 mmol) were used following general procedure B for 1 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3af** after flash chromatography on silica gel (eluent: 40% ethyl acetate in hexanes) as a pale-yellow oil with a 2:1 E/Z ratio (306 mg, 88%). Analytical TLC: R_f = 0.48 (100% ethyl acetate). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 6.11 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 4.9 Hz, 0.65H), 5.96 (ddt, $^3J_{HH}$ = 11.5 Hz, $^4J_{HP}$ = 4.2 Hz, $^4J_{HH}$ = 1.2 Hz, 0.35H), 5.59 (ddt, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.65H), 5.48 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 7.8 Hz, 0.35H), 5.03 (s, 0.35H), 5.00 (s, 0.35H), 4.94 (s, 0.65H), 4.91 (s, 0.65H), 4.12−3.95 (m, 4H), 3.65 (t, $^3J_{HH}$ = 7.2 Hz, 1.3H), 3.59 (t, $^3J_{HH}$ = 7.0 Hz, 0.7H), 2.75 (ddd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 0.7H), 2.58 (dd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 7.6 Hz, 1.3H), 2.37 (t, $^3J_{HH}$ = 7.2 Hz, 1.3H), 2.24 (t, $^3J_{HH}$ = 6.9 Hz, 0.7H), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 2.1H), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3.9H), 0.82 (s, 5.85H), 0.81 (s, 3.15H), −0.02 (s, 3.9H), −0.03 (s, 2.1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 142.3 (d, $^4J_{CP}$ = 4.2 Hz), 141.5 (d, $^4J_{CP}$ = 3.6 Hz), 136.9 (d, $^3J_{CP}$ = 14.7 Hz), 134.2 (d, $^3J_{CP}$ = 14.7 Hz), 119.8 (d, $^2J_{CP}$ = 10.8 Hz), 118.2 (d, $^2J_{CP}$ = 12.0 Hz), 116.8 (d, $^5J_{CP}$ = 4.0 Hz), 116.0 (d, $^5J_{CP}$ = 2.8 Hz), 62.2, 62.0, 61.9 (d, $^2J_{CP}$ = 6.7 Hz), 61.8 (d, $^2J_{CP}$ = 6.7 Hz), 40.4, 35.7, 30.9 (d, $^1J_{CP}$ = 139.0 Hz), 27.1 (d, $^1J_{CP}$ = 140.2 Hz), 26.0, 25.9, 18.32, 18.27, 16.47 (d, $^3J_{CP}$ = 5.9 Hz), 16.45 (d, $^3J_{CP}$ = 6.0 Hz), −5.27, −5.30. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 27.15 (s, minor), 26.50 (s, major). FT-IR (neat, cm^{-1}): 3456, 2954, 2929, 2904, 2857, 2084, 1737, 1607, 1472, 1463, 1444, 1390, 1362, 1251, 1164, 1095, 1054, 1025, 963, 890, 834, 812, 775, 731, 663, 523. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{35}O_4PSiNa$ 385.1934, found 385.1927.

*5-(Diethoxyphosphoryl)-2-methylene-1-phenylpent-3-en-1-yl Acetate (**3ag**).* Compounds **1a** (269 mg, 1.51 mmol), (±)-**2g** (87 mg, 0.50 mmol), and **Ru3** (17 mg, 0.026 mmol) were used following general procedure B for 1 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3ag** after flash chromatography on silica gel (eluent: 5% to 10% ethanol in hexanes) as a pale-yellow oil with a 2:1 E/Z ratio (148 mg, 84%). Analytical TLC: R_f = 0.26 (10% ethanol in hexanes). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.41−7.26 (m, 5H), 6.51 (s, 0.65H), 6.21 (s, 0.35H), 6.12 (dd, $^3J_{HH}$ = 16.2 Hz, $^4J_{HP}$ = 5.1 Hz, 0.65H), 5.93 (dd, $^3J_{HH}$ = 11.4 Hz, $^4J_{HP}$ = 3.4 Hz, 0.35H), 5.76−5.53 (m, 1H), 5.41 (s, 0.35H), 5.34 (s, 0.35H), 5.29 (s, 1.3H), 4.13−3.83 (m, 4H), 2.84−2.62 (m, 0.7H), 2.56 (dd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 7.5 Hz, 1.3H), 2.12 (s, 1H), 2.11 (s, 2H), 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 2.1H), 1.22 (t, $^3J_{HH}$ = 7.0 Hz, 3.9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 169.78, 169.76, 143.4 (d, $^4J_{CP}$ = 4.1 Hz), 142.3 (d, $^4J_{CP}$ = 3.3 Hz), 138.2, 138.1, 133.3 (d, $^3J_{CP}$ = 14.8 Hz), 130.1 (d, $^3J_{CP}$ = 14.7 Hz), 128.51, 128.46, 128.3, 128.2, 127.6, 127.2, 122.7 (d, $^2J_{CP}$ = 10.6 Hz), 120.9 (d, $^2J_{CP}$ = 11.8 Hz), 116.1 (d, $^5J_{CP}$ = 3.8 Hz), 115.7 (d, $^5J_{CP}$ = 2.9 Hz), 77.5 (d, $^5J_{CP}$ = 1.8 Hz), 74.9, 62.01 (d, $^2J_{CP}$ = 6.7 Hz), 61.95 (d, $^2J_{CP}$ = 6.5 Hz), 61.9 (d, $^2J_{CP}$ = 6.8 Hz), 31.2 (d, $^1J_{CP}$ = 138.6 Hz), 27.2 (d, $^1J_{CP}$ = 140.1 Hz), 21.20, 21.19, 16.5 (d, $^3J_{CP}$ = 6.0 Hz), 16.4 (d, $^3J_{CP}$ = 5.9 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.81 (s, minor), 25.78 (s, major). FT-IR (neat, cm^{-1}): 2982, 2931, 1739, 1647, 1495, 1455, 1392, 1370, 1228, 1163, 1097, 1021, 961, 865, 847, 761, 700, 607, 536. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{25}O_5PNa$ 375.1332, found 375.1343.

*(E)-tert-Butyldimethyl((1-phenylpent-1-en-4-yn-3-yl)oxy)silane (**2h**).* Alkynol **2h** was prepared using a modified procedure from the literature.[50] Trimethylsilylacetylene (4.30 mL, 31.0 mmol) was added to a 250 mL rb flask and was subsequently dissolved in THF (ca. 0.38 M). The flask was then cooled to −78 °C, and *n*-butyllithium (11.0 mL, 2.2 M in hexanes, 24.2 mmol) was added dropwise. The reaction mixture was allowed to stir for 30 min, and a solution of cinnamaldehyde (2.55 g, 19.3 mmol) in THF (10 mL) was added dropwise. The reaction mixture was then allowed to stir for an additional 30 min and was warmed to 0 °C. K_2CO_3 (700 mg, 5.06 mmol) in methanol (40 mL) was then added, and the reaction mixture was allowed to stir and warm to room temperature overnight. A saturated aqueous solution of NH_4Cl (40 mL) was then added, and the organic layer was removed. The aqueous layer was then extracted with Et_2O (3×, 40 mL) and the organic layers were combined. The organic layer was then extracted with water (80 mL) and brine (80 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated via rotatory evaporation and passed through a silica plug (eluent: 10% ethyl acetate in hexanes). This afforded the alcohol as a clear yellow oil (2.34 g, 77%). Analytical TLC: R_f = 0.25 (20% ethyl acetate in hexanes). Spectral data match the literature report.[50]

The alcohol (790 mg, 4.99 mmol) was added to a 100 mL rb flask and was subsequently dissolved in CH_2Cl_2 (ca. 0.13 M). The flask was then cooled to 0 °C, and DMAP (37 mg, 0.29 mmol), diisopropylethylamine (4.40 mL, 25.3 mmol), and TBSCl (1.58 g, 10.5 mmol) were added. The reaction mixture was then allowed to stir and warm to room temperature overnight. A saturated aqueous solution of NH_4Cl (20 mL) was then added, and the organic layer was removed. The aqueous layer was then extracted with CH_2Cl_2 (3×, 20 mL), and the organic layers were combined. The organic layer was then extracted with water (40 mL) and brine (40 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated via rotatory evaporation and purified by flash column chromatography on silica gel (eluent: 15% to 20% ethyl acetate in hexanes) to afford **2h** as a clear yellow oil (1.23 g, 90%). Analytical TLC: 0.60 (20% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.43−7.37 (m, 2H), 7.35−7.29 (m, 2H), 7.28−7.22 (m, 1H), 6.72 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 6.25 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 5.6 Hz, 1H), 5.08 (ddd, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 2.56 (d, $^3J_{HH}$ = 2.2 Hz, 1H), 0.96 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 136. 6, 130.7, 129.0, 128.7, 128.0, 126. 9, 83.7, 73. 7, 63.5, 26.0, 18.5, −4.4, −4.6. FT-IR (neat, cm^{-1}): 3308, 3028, 2955, 2930, 2886, 2857, 1737, 1601, 1578, 1496, 1472, 1463, 1449, 1390, 1362, 1297, 1252, 1204, 1113, 1060, 1005, 964, 939, 909, 870, 834, 812, 778, 733, 692, 651, 580, 554. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{24}OSiNa$ 295.1489, found 295.1494.

*Diethyl ((6E)-5-((tert-**b**utyldimethylsilyl)oxy)-4-methylene-7-phenylhepta-2,6-dien-1-yl)phosphonate (**3ah**).* Compounds **1a** (140 mg, 0.78 mmol), (±)-**2h** (70 mg, 0.26), and **Ru3** (8 mg, 0.012 mmol) were used following general procedure B for 1 h. The catalyst was quenched with ethyl vinyl ether, which afforded **3ah** after flash chromatography on silica gel (eluent: 40% ethyl acetate in hexanes) as a dark-brown oil with a 1.5:1 E/Z ratio (96 mg, 84%). Analytical TLC: R_f = 0.77 (100% ethyl acetate). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.38−7.33 (m, 2H), 7.32−7.25 (m, 2H), 7.24−7.17 (m, 1H), 6.59 (d, $^3J_{HH}$ = 16.0 Hz, 0.6H), 6.55 (d, $^3J_{HH}$ = 16.0 Hz, 0.4H), 6.18

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(dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 5.8 Hz, 0.6H), 6.16−6.10 (m, 1H), 6.11 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 5.9 Hz, 0.4H), 5.89 (ddt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.2 Hz, 0.6H), 5.65 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.4H), 5.39 (s, 0.4H), 5.29 (s, 0.6H), 5.22 (s, 0.4H), 5.13 (s, 0.6H), 4.96 (d, $^3J_{HH}$ = 5.7 Hz, 0.6H), 4.72 (d, $^3J_{HH}$ = 5.9 Hz, 0.4H), 4.15−3.95 (m, 4H), 2.90−2.70 (m, 0.8H), 2.63 (ddd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1.2H), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 1.2H), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 1.2H), 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 1.8H), 1.20 (t, $^3J_{HH}$ = 7.1 Hz, 1.8H), 0.93 (s, 5.4H), 0.92 (s, 3.6H), 0.09 (s, 2H), 0.08 (s, 2H), 0.08 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 147.2 (d, $^4J_{CP}$ = 4.0 Hz), 145.7 (d, $^4J_{CP}$ = 3.4 Hz), 137.04, 137.01, 133.5 (d, $^3J_{CP}$ = 15.0 Hz), 131.8, 131.4, 130.9 (d, $^3J_{CP}$ = 14.7 Hz), 129.8, 129.7, 128.6, 128.6, 127.6, 127.5, 126.59, 126.57, 121.6 (d, $^2J_{CP}$ = 10.6 Hz), 119.9 (d, $^2J_{CP}$ = 11.8 Hz), 114.2 (d, $^5J_{CP}$ = 3.6 Hz), 113.8 (d, $^5J_{CP}$ = 2.8 Hz), 76.6 (d, $^5J_{CP}$ = 1.8 Hz), 74.2 (d, $^5J_{CP}$ = 0.8 Hz), 62.1 (d, $^2J_{CP}$ = 6.5 Hz), 62.04 (d, $^2J_{CP}$ = 6.5 Hz), 61.97 (d, $^2J_{CP}$ = 6.6 Hz), 61.96 (d, $^2J_{CP}$ = 6.7 Hz), 31.5 (d, $^1J_{CP}$ = 138.6 Hz), 27.5 (d, $^1J_{CP}$ = 140.3 Hz), 25.96, 25.94, 18.5, 16.53 (d, $^3J_{CP}$ = 4.5 Hz), 16.51 (d, $^3J_{CP}$ = 5.8 Hz), 16.48 (d, $^3J_{CP}$ = 4.4 Hz), 16.46 (d, $^3J_{CP}$ = 5.7 Hz), −4.58, −4.65, −4.72, −4.73. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 27.16 (s, minor), 26.36 (s, major). FT-IR (neat, cm^{-1}): 3027, 2955, 2929, 2901, 2857, 2103, 1601, 1495, 1472, 1463, 1448, 1390, 1361, 1250, 1163, 1099, 1055, 1025, 962, 904, 881, 833, 814, 776, 747, 693, 590, 532. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{39}O_4PSiNa$ 473.2247, found 473.2247.

*Diethyl (4-(Trimethylsilyl)penta-2,4-dien-1-yl)phosphonate (**3ai**).* Compounds **1a** (294 mg, 1.65 mmol), **2i** (52 mg, 0.52 mmol), and **Ru3** (17 mg, 0.026) were used following general procedure B for 1 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3ai** after flash chromatography on silica gel (eluent: ethyl acetate) as a pale-yellow oil with a 9:1 E/Z ratio (107 mg, 74%). Analytical TLC: R_f = 0.39 (100% ethyl acetate). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 6.20 (dd, $^3J_{HH}$ = 15.9, $^4J_{HP}$ = 5.1 Hz, 0.9H), 6.17−6.12 (m, 0.1H), 5.62−5.60 (m, 0.9H), 5.59 (ddt, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 7.3 Hz, 0.9H), 5.46−5.44 (m, 0.1H), 5.43 (ddt, $^3J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 0.1H), 5.34−5.29 (m, 1H), 4.13−3.96 (m, 4H), 2.64 (ddd, $^2J_{HP}$ = 22.1 Hz, $^3J_{HH}$ = 7.7 Hz, $^2J_{HH}$ = 1.6 Hz, 0.2H), 2.57 (ddd, $^2J_{HP}$ = 22.1 Hz, $^3J_{HH}$ = 7.5 Hz, $^2J_{HH}$ = 1.5 Hz, 1.8H), 1.25 (t, $^3J_{HH}$ = 7.0 Hz, 0.6H), 1.24 (t, $^3J_{HH}$ = 7.1 Hz, 5.4H), 0.10 (s, 8.1H), 0.02 (s, 0.9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 148.8 (d, $^4J_{CP}$ = 3.1 Hz), 148.4 (d, $^4J_{CP}$ = 3.8 Hz), 139.5 (d, $^3J_{CP}$ = 14.8 Hz), 135.4 (d, $^3J_{CP}$ = 14.8 Hz), 127.8 (d, $^5J_{CP}$ = 4.2 Hz), 126.7 (d, $^5J_{CP}$ = 3.9 Hz), 120.4 (d, $^2J_{CP}$ = 12.2 Hz). 117.5 (d, $^2J_{CP}$ = 10.4 Hz), 61.9 (d, $^2J_{CP}$ = 6.6 Hz), 61.7 (d, $^2J_{CP}$ = 6.7 Hz), 31.2 (d, $^1J_{CP}$ = 138.6 Hz), 26.4 (d, $^1J_{CP}$ = 140.6 Hz), 16.4 (d, $^3J_{CP}$ = 5.9 Hz), 16.3 (d, $^3J_{CP}$ = 6.3 Hz), −1.0, −2.1. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 27.58 (s, minor), 26.52 (s, major). FT-IR (neat, cm^{-1}): 3463, 2981, 2957, 2904, 2100, 1723, 1635, 1479, 1444, 1393, 1368, 1295, 1248, 1164, 1098, 1024, 962, 837, 800, 759, 721, 692, 655, 618, 527. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{25}O_3PSiNa$ 299.1203, found 299.1208.

*tert-Butyl (5-(Diethoxyphosphoryl)-2-methylenepent-3-en-1-yl)-(tosyl)carbamate (**3aj**).* Compounds **1a** (272 mg, 1.53 mmol), **2j** (156 mg, 0.50 mmol), and **Ru3** (16 mg, 0.026 mmol) were used following general procedure B for 1 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3aj** after flash chromatography on silica gel (eluent: ethyl acetate) as a pale-yellow oil with a 1.5:1 E/Z ratio (232 mg, 95%). Analytical TLC: R_f = 0.28 (100% ethyl acetate). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.85−7.78 (m, 2H), 7.34−7.28 (m, 2H), 6.29 (dd, $^3J_{HH}$ = 16.1 Hz, $^4J_{HP}$ = 4.8 Hz, 0.6H), 6.08 (ddd, $^3J_{HH}$ = 11.4 Hz, $^4J_{HP}$ = 4.4 Hz, $^4J_{HH}$ = 1.0 Hz, 0.4H), 5.70 (ddt, $^3J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 7.6 Hz, 0.6H), 5.69 (ddd, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HP}$ = 6.8 Hz, 0.4H), 5.30 (s, 0.4H), 5.26 (s, 0.4H), 5.57 (s, 0.6H), 5.08 (s, 0.6H), 4.63 (s, 1.2H), 4.46 (s, 0.8H), 4.18−4.05 (m, 4H), 2.82 (ddd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 8.0 Hz, $^2J_{HH}$ = 1.5 Hz, 0.8H), 2.67 (ddd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 0.9 Hz, 1.2H), 2.45 (s, 1.8H), 2.44 (s, 1.2H), 1.35 (s, 3.6H), 1.35 (s, 5.4H), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 2.4H), 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3.6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 150.80, 150.78, 144.4, 144.3, 140.3 (d, $^4J_{CP}$ = 3.9 Hz), 139.8 (d, $^4J_{CP}$ = 3.6 Hz), 137.1, 137.0, 134.7 (d, $^3J_{CP}$ = 14.8 Hz), 131.2 (d, $^3J_{CP}$ = 14.5 Hz), 129.22, 129.21, 128.3, 128.2, 122.4 (d, $^2J_{CP}$ = 10.9 Hz), 118.9 (d, $^2J_{CP}$ = 11.5 Hz), 115.3 (d, $^5J_{CP}$ = 3.0 Hz), 114.6 (d, $^5J_{CP}$ = 3.9 Hz), 84.37, 84.35, 62.1 (d, $^2J_{CP}$ = 6.8 Hz), 62.0 (d, $^2J_{CP}$ = 6.5 Hz), 50.8 (d, $^5J_{CP}$ = 2.3 Hz), 47.8, 31.2 (d, $^1J_{CP}$ = 139.2 Hz), 27.9, 27.8, 27.3 (d, $^1J_{CP}$ = 139.8 Hz), 21.65, 21.65, 16.50 (d, $^3J_{CP}$ = 6.0 Hz), 16.47 (d, $^3J_{CP}$ = 6.0 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.59 (s, minor), 25.94 (s, major). FT-IR (neat, cm^{-1}): 3453, 2981, 2933, 2103, 1728, 1644, 1597, 1495, 1478, 1443, 1394, 1355, 1285, 1248, 1187, 1148, 1090, 1024, 962, 939, 849, 806, 772, 718, 675, 659, 591, 545. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{34}NO_7PSNa$ 510.1686, found 510.1701.

*Diethyl (6-(1,3-Dioxoisoindolin-2-yl)-4-methylenehex-2-en-1-yl)-phosphonate (**3ak**).* Compounds **1a** (137 mg, 0.77 mmol), **2b** (50 mg, 0.25 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure B for 1 h. The catalyst was quenched with ethyl vinyl ether, which afforded **3ak** after flash chromatography on silica gel (eluent: 5% to 10% ethanol in hexanes) as a dark-brown oil with a 1:1 E/Z ratio (71 mg, 75%). Analytical TLC: R_f = 0.23 (10% ethanol in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84−7.76 (m, 2H), 7.71−7.65 (m, 2H), 6.17 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 4.6 Hz, 0.5H), 6.05 (dd, $^3J_{HH}$ = 11.4 Hz, $^4J_{HP}$ = 3.2 Hz, 0.5H), 5.79 (ddt, $^3J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.5H), 5.55 (ddt, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.4 Hz, 0.5H), 5.10 (s, 0.5H), 5.05 (s, 0.5H), 4.98 (s, 0.5H), 4.96 (s, 0.5H), 4.16−3.95 (m, 4H), 3.80 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 3.75 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 2.77 (dd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 7.9 Hz, 1H), 2.65 (dd, $^2J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 2.56 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 2.46 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 1.30 (t, $^3J_{HH}$ = 7.0 Hz, 3H), 1.27 (t, $^3J_{HH}$ = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 168.23, 168.22, 142.0 (d, $^4J_{CP}$ = 4.3 Hz), 140. Eight (d, $^4J_{CP}$ = 3.6 Hz), 136.0 (d, $^3J_{CP}$ = 14.8 Hz), 134.00, 133.98, 133.3 (d, $^3J_{CP}$ = 14.6 Hz), 132.2, 132.1, 123.3 (2 C), 121.0 (d, $^2J_{CP}$ = 11.0 Hz), 119.1 (d, $^2J_{CP}$ = 12.0 Hz), 117.3 (d, $^5J_{CP}$ = 4.3 Hz), 116.9 (d, $^5J_{CP}$ = 2.8 Hz), 62.1 (d, $^2J_{CP}$ = 6.7 Hz), 62.0 (d, $^2J_{CP}$ = 6.7 Hz), 37.1, 36.9, 35.7, 31.1, 30.9 (d, $^1J_{CP}$ = 138.8 Hz), 27.3 (d, $^1J_{CP}$ = 140.2 Hz), 16.6 (d, $^3J_{CP}$ = 5.6 Hz), 16.5 (d, $^3J_{CP}$ = 5.5 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.86 (s, 0.5P), 26.22 (s, 0.5P). FT-IR (neat, cm^{-1}): 3464, 2981, 2933, 2103, 1772, 1709, 1613, 1467, 1439, 1394, 1361, 1297, 1247, 1188, 1163, 1099, 1023, 961, 870, 793, 720, 629, 530. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NO_5PNa$ 400.1283, found 400.1295.

*Methyl (Z)-5-(Diethoxyphosphoryl)-2-methylenepent-3-enoate (**3al**).* Compounds **1a** (269 mg, 1.51 mmol), **2l** (44 mg, 0.53 mmol), and **Ru3** (16 mg, 0.025 mmol) were used following general procedure B for 1 h. The catalyst was quenched with ethyl vinyl ether, which afforded **3al** after flash chromatography on silica gel (eluent: 5% to 10% ethanol in hexanes) as a dark-brown oil as the Z-isomer only (72 mg, 52%). Analytical TLC: R_f = 0.11 (10% ethanol in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 6.37 (s, 1H), 5.91 (dddt, $^3J_{HH}$ = 11.6 Hz, $^4J_{HP}$ = 4.9 Hz, $^4J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 5.96 (s, 1H), 5.71 (ddt, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HP}$ = 6.4 Hz, 1H), 4.15−3.98 (m, 4H), 3.73 (s, 3H), 2.71 (ddd, $^2J_{HP}$ = 22.6 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.6 Hz, 2H), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 166.8 (d, $^5J_{CP}$ = 2.0 Hz), 135.1 (d, $^4J_{CP}$ = 3.5 Hz), 128.6 (d, $^3J_{CP}$ = 14.5 Hz), 128.3 (d, $^5J_{CP}$ = 2.9 Hz), 122. Seven (d, $^2J_{CP}$ = 11.0 Hz), 62.1 (d, $^2J_{CP}$ = 6.6 Hz), 52.2, 27.1 (d, $^1J_{CP}$ = 140.1 Hz), 16.5 (d, $^3J_{CP}$ = 6.0 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 26.27 (s). FT-IR (neat, cm^{-1}): 3444, 2983, 2954, 2910, 2088, 1720, 1641, 1614, 1438, 1392, 1369, 1302, 1245, 1198, 1161, 1139, 1097, 1051, 1023, 960, 879, 844, 815, 768, 709, 636. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{19}O_5PNa$ 285.0862, found 285.0868.

*Dimethyl (6-((tert-Butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl)phosphonate (**3bf**).* Compounds **1b** (225 mg, 1.50 mmol), **2f** (94 mg, 0.51 mmol), and **Ru3** (16 mg, 0.026 mmol) were used following general procedure B for 1 h. The catalyst was quenched with ethyl vinyl ether, which afforded **3bf** after flash chromatography on silica gel (eluent: 70% to 100% ethyl acetate in hexanes) as a dark-brown oil with a 1.5:1 E/Z ratio (95 mg, 56%). Analytical TLC: R_f =

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0.43 (100% ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.15 (ddt, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 4.9 Hz, $^4J_{HH}$ = 1.1 Hz, 0.6H), 6.00 (ddt, $^3J_{HH}$ = 11.5 Hz, $^4J_{HP}$ = 4.4 Hz, $^4J_{HH}$ = 1.6 Hz, 0.4H), 5.60 (ddt, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 0.6H), 5.49 (ddt, $^3J_{HH}$ = 11.5, $^3J_{HH}$ = 7.9 Hz, $^3J_{HP}$ = 7.0 Hz, 0.4H), 5.04 (s, 0.4H), 5.03 (s, 0.4H), 4.98 (s, 0.6H), 5.94 (s, 0.6H), 3.71 (d, $^3J_{HP}$ = 10.9 Hz, 2.4H), 3.70 (d, $^3J_{HP}$ = 10.9 Hz, 3.6H), 3.68 (d, $^3J_{HH}$ = 7.2 Hz, 1.2H), 3.62 (d, $^3J_{HH}$ = 7.0 Hz, 0.8H), 2.79 (ddd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, 0.8H), 2.39 (ddd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1.2H), 2.39 (t, $^3J_{HH}$ = 7.2 Hz, 1.2H), 2.26 (d, $^3J_{HH}$ = 7.0 Hz, 0.8H), 0.84 (s, 5.4H), 0.83 (s, 3.6H), −0.00 (s, 3.6H), −0.01 (s, 2.4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 142.3 (d, $^4J_{CP}$ = 4.2 Hz), 141.5 (d, $^4J_{CP}$ = 3.6 Hz), 137.2 (d, $^3J_{CP}$ = 14.8 Hz), 134.6 (d, $^3J_{CP}$ = 14.7 Hz), 119.4 (d, $^2J_{CP}$ = 10.9 Hz), 117.8 (d, $^2J_{CP}$ = 12.1 Hz), 117.1 (d, $^5J_{CP}$ = 3.9 Hz), 116.1 (d, $^5J_{CP}$ = 2.8 Hz), 62.3, 62.0, 52.8 (d, $^2J_{CP}$ = 6.6 Hz), 52.7 (d, $^2J_{CP}$ = 6.7 Hz), 40.4 (d, $^5J_{CP}$ = 1.6 Hz), 35.6, 29.9 (d, $^1J_{CP}$ = 139.2 Hz), 26.2 (d, $^1J_{CP}$ = 140.1 Hz), 26.01, 25.97, 18.4, 18.3, −5.2, −5.26. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 29.64 (s, minor), 28.94 (s, major). FT-IR (neat, cm^{-1}): 2953, 2929, 2896, 2856, 1723, 1607, 1472, 1463, 1389, 1361, 1253, 1174, 1095, 1057, 1029, 967, 936, 888, 832, 811, 775, 724, 663, 520. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{31}O_4PSiNa$ 357.1621, found 357.1623.

*tert-Butyl (5-(Dimethoxyphosphoryl)-2-methylenepent-3-en-1-yl)(tosyl)carbamate (**3bj**).* Compounds **1b** (226 mg, 1.50 mmol), **2j** (155 mg, 0.50 mmol), and **Ru3** (16 mg, 0.026 mmol) were used following general procedure B for 1 h. The catalyst was quenched with ethyl vinyl ether, which afforded **3bj** after flash chromatography on silica gel (eluent: 5% to 10% ethanol in hexanes) as a dark-brown oil with a 1.2:1 E/Z ratio (185 mg, 80%). Analytical TLC: R_f = 0.13 (10% ethanol in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84−7.77 (m, 2H), 7.35−7.27 (m, 2H), 6.23 (dd, $^3J_{HH}$ = 16.0 Hz, $^3J_{HP}$ = 4.7 Hz, 0.55H), 6.09 (ddt, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 3.6 Hz, $^4J_{HH}$ = 1.3 Hz, 0.45H), 5.74−5.63 (m, 1H), 5.27 (s, 0.45H), 5.26 (0.45H), 5.17 (s, 0.55H), 5.10 (s, 0.55H), 4.64 (s, 1.1H), 4.46 (s, 0.9H), 3.77 (d, $^3J_{HP}$ = 10.9 Hz, 2.7H), 3.76 (d, $^3J_{HP}$ = 10.8 Hz, 3.3H), 2.85 (ddd, $^2J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 0.9H), 2.69 (dd, $^2J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 7.5 Hz, 1.1H), 2.45 (s, 1.65H), 2.45 (s, 1.35H), 1.36 (s, 4.95H), 1.35 (s, 4.05H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 150.79, 150.77, 144.4, 144.3, 140.3 (d, $^4J_{CP}$ = 3.9 Hz), 139.8 (d, $^4J_{CP}$ = 3.6 Hz), 137.1, 137.0, 134.9 (d, $^3J_{CP}$ = 14.9 Hz), 131.5 (d, $^3J_{CP}$ = 14.6 Hz), 129.23 129.22, 128.22, 128.17, 122.0 (d, $^2J_{CP}$ = 11.0 Hz), 118.5 (d, $^2J_{CP}$ = 11.9 Hz), 115.4 (d, $^5J_{CP}$ = 2.7 Hz), 114.9 (d, $^5J_{CP}$ = 3.6 Hz), 84.42, 84.38, 52.8 (d, $^2J_{CP}$ = 6.1 Hz), 52.7 (d, $^2J_{CP}$ = 6.1 Hz), 50.8 (d, $^5J_{CP}$ = 2.3 Hz), 47.8, 30.2 (d, $^1J_{CP}$ = 139.4 Hz), 27.9, 27.8, 26.3 (d, $^1J_{CP}$ = 139.8 Hz), 21.65, 21.65. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 29.07 (s, minor), 28.38 (s, major). FT-IR (neat, cm^{-1}): 2981, 2954, 2852, 1728, 1597, 1495, 1456, 1396, 1354, 1251, 1187, 1153, 1089, 1030, 937, 881, 848, 8076, 771, 720, 675, 591, 545. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{20}H_{30}NO_7PSNa$ 482.1373, found 482.1385.

*6-(Bis(2,2,2-trifluoroethoxy)phosphoryl)-3-methylenehex-4-en-2-yl Benzoate (**3cb**).* Compounds **1c** (145 mg, 0.51 mmol), (±)-**2b** (89 mg, 0.51 mmol), and **Ru2A** (16 mg, 0.025 mmol) were used following general procedure A (ca. 0.10 M). The catalyst was quenched with ethyl vinyl ether, which afforded **3cb** after flash chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) as a pale-yellow oil with a 1.5:1 E/Z ratio (208 mg, 89%). Analytical TLC: R_f: 0.38 and 0.29 for the Z and E-isomer, respectively (20% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.07−8.00 (m, 2H), 7.58−7.50 (m, 1H), 7.45−7.40 (m, 2H), 6.28−6.24 (m, 0.4H), 6.25 (ddd, $^3J_{HH}$ = 15.9 Hz, $^4J_{HP}$ = 5.8 Hz, $^4J_{HH}$ = 0.6 Hz, 0.6H), 5.78 (ddt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.4 Hz, 0.6H), 5.77 (q, $^3J_{HH}$ = 6.6 Hz, 0.6H), 5.49 (ddt, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.4H), 5.53 (q, $^3J_{HH}$ = 6.6 Hz, 0.4H), 5.39 (s, 0.4H), 5.33 (s, 0.6H), 5.19−5.16 (m, 1H), 5.17 (s, 0.5H), 4.40−4.26 (m, 4H), 3.07−2.89 (m, 0.8H), 2.81 (ddd, $^2J_{HP}$ = 23.1 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.7 Hz, 1.2H), 1.83 (d, $^3J_{HH}$ = 6.6 Hz, 1.8H), 1.43 (d, $^3J_{HH}$ = 6.6 Hz, 1.2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 165.60, 165.59, 145.4 (d, $^4J_{CP}$ = 4.8 Hz), 143.8 (d, $^4J_{CP}$ = 3.7 Hz), 135.5 (d, $^3J_{CP}$ = 15.6 Hz), 133.0 (s), 132.3 (d, $^3J_{CP}$ = 15.8 Hz), 130.4, 130.3, 129.60, 129.56, 128.4, 122.60 (dq, $^1J_{CF}$ = 275.8 Hz, $^3J_{CP}$ = 7.7 Hz), 122.58 (dq, $^1J_{CF}$ = 275.8 Hz, $^3J_{CP}$ = 7.5 Hz), 119.8 (d, $^2J_{CP}$ = 11.4 Hz), 116.8 (d, $^2J_{CP}$ = 13.1 Hz), 115.8 (d, $^5J_{CP}$ = 4.3 Hz), 115.1 (d, $^5J_{CP}$ = 1.9 Hz), 73.0 (d, $^5J_{CP}$ = 2.1 Hz), 70.3, 63.2−61.2 (m), 30.7 (d, $^1J_{CP}$ = 140.7 Hz), 26.9 (d, $^1J_{CP}$ = 142.1 Hz), 20.1, 19.6. [Note: The multiplet reported at δ_C 63.2−61.2 ppm appears as complex overlap of two doublet-of-quartets expected to be observed from the methylene carbon in the 2,2,2-trifluoroethoxy moiety for both E and Z-isomers. An expansion is provided within its spectrum.] ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 30.06 (s, minor), 29.26 (s, major). FT-IR (neat, cm^{-1}): 2972, 2252, 1715, 1603, 1585, 1492, 1452, 1418, 1377, 1264, 1168, 1104, 1069, 1026, 963, 909, 881, 843, 733, 712, 688, 658, 649, 555, 518. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{18}H_{19}F_6O_5PNa$ 483.0766, found 483.0780.

*Bis(2,2,2-trifluoroethyl) (5-((tert-butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl)phosphonate (**3cd**).* Compounds **1c** (216 mg, 0.75 mmol), (±)-**2d** (47 mg, 0.25 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with ethyl vinyl ether, which afforded **3 cd** after flash chromatography on silica gel (eluent: 15% ethyl acetate in hexanes) as a pale-yellow oil with a 1.2:1 E/Z ratio (88 mg, 74%). Analytical TLC: R_f = 0.35 and 0.29 for the Z and E-isomer, respectively (20% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.23−6.17 (m, 0.45H), 6.18 (ddd, $^3J_{HH}$ = 16.0 Hz, $^3J_{HP}$ = 5.5 Hz, $^4J_{HH}$ = 0.6 Hz, 0.55H), 5.68 (ddt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 0.55H), 5.57 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.45H), 5.28 (s, 0.45H), 5.22 (s, 0.55H), 5.02 (s, 0.55H), 5.00 (s, 0.45H), 4.46 (q, $^3J_{HH}$ = 6.4 Hz, 0.55H), 4.43−4.31 (m, 4H), 4.24 (q, $^3J_{HH}$ = 6.3 Hz, 0.45H), 3.05−2.88 (m, 0.9H), 2.79 (ddd, $^2J_{HP}$ = 22.9 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.6 Hz, 1.1H), 1.25 (d, $^3J_{HH}$ = 6.4 Hz, 1.65H), 1.16 (d, $^3J_{HH}$ = 6.4 Hz, 1.35H), 0.87 (s, 4.05H), 0.87 (s, 4.95H), 0.04 (s, 1.35H), 0.03 (s, 1.65H), 0.02 (s, 1.35H), −0.0 (s, 1.65H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 149.6 (d, $^4J_{CP}$ = 4.7 Hz), 148.1 (d, $^4J_{CP}$ = 3.7 Hz), 136.6 (d, $^3J_{CP}$ = 15.8 Hz), 133.4 (d, $^3J_{CP}$ = 15.9 Hz), 122.67 (dq, $^1J_{CF}$ = 275.8 Hz, $^3J_{CP}$ = 7.6 Hz), 122.66 (dq, $^1J_{CF}$ = 275.9 Hz, $^3J_{CP}$ = 7.6 Hz), 118.3 (d, $^2J_{CP}$ = 11.3 Hz), 115.8 (d, $^2J_{CP}$ = 13.1 Hz), 114.2 (d, $^5J_{CP}$ = 4.3 Hz), 112.9 (d, $^5J_{CP}$ = 3.0 Hz), 71.5 (d, $^5J_{CP}$ = 2.0 Hz), 69.2, 62.4 (dq, $^2J_{CF}$ = 37.8 Hz, $^2J_{CP}$ = 6.2 Hz), 62.28 (dq, $^2J_{CF}$ = 37.7 Hz, $^2J_{CP}$ = 6.3 Hz), 62.24 (dq, $^2J_{CF}$ = 37.7 Hz, $^2J_{CP}$ = 6.3 Hz), 30.9 (d, $^1J_{CP}$ = 140.5 Hz), 27.2 (d, $^1J_{CP}$ = 142.2 Hz), 26.9, 24.6, 23.7, 18.3, −4.85, −4.93, −5.1. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 30.39 (s, minor), 29.55 (s, major). FT-IR (neat, cm^{-1}): 2958, 2932, 2859, 2253, 1721, 1473, 1417, 1299, 1258, 1174, 1106, 1074, 964, 906, 836, 777, 730, 650, 554, 518. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{29}F_6O_4PSiNa$ 493.1385, found 493.1369.

*Bis(2,2,2-trifluoroethyl) ((6E)-5-((tert-Butyldimethylsilyl)oxy)-4-methylene-7-phenylhepta-2,6-dien-1-yl)phosphonate (**3ch**).* Compounds **1c** (432 mg, 1.51 mmol), (±)-**2h** (153 mg, 0.56 mmol), and **Ru3** (17 mg, 0.026 mmol) were used following general procedure A (ca. 0.05M). The catalyst was quenched with ethyl vinyl ether, which afforded **3ch** after flash chromatography on silica gel (eluent: 15% ethyl acetate in hexanes) as a pale-yellow oil with a 1.3:1 E/Z ratio (250 mg, 80%). Analytical TLC: R_f = 0.17 and 0.15 for the Z and E-isomer, respectively (15% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.38−7.34 (m, 2H), 7.32−7.27 (m, 2H), 7.24−7.18 (m, 1H), 6.60 (dd, $^3J_{HH}$ = 16.0 Hz, J = 1.1 Hz, 0.57H), 6.57 (dd, $^3J_{HH}$ = 15.8 Hz, J = 0.7 Hz, 0.43H), 6.22 (ddt, $^3J_{HH}$ = 11.7 Hz, $^4J_{HP}$ = 4.4 Hz, $^4J_{HH}$ = 1.3 Hz, 0.43H), 6.20 (ddt, $^3J_{HH}$ = 16.1 Hz, $^4J_{HP}$ = 5.2 Hz, $^4J_{HH}$ = 0.5 Hz, 0.57H), 6.17 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 5.8 Hz, 0.57H), 6.11 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.0 Hz, 0.43H), 5.86 (ddt, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 0.57H), 5.58 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 0.43H), 5.43 (s, 0.43H), 5.35 (s, 0.57H), 5.17 (d, J = 1.7 Hz, 0.57H), 5.17 (s, 0.43H), 4.97 (d, $^3J_{HH}$ = 5.8 Hz, 0.57H), 4.74 (d, $^3J_{HH}$ = 5.9 Hz, 0.43H), 4.40−4.16 (m, 4H), 3.08−2.88 (m, 0.86H), 2.78 (ddd, $^2J_{HP}$ = 23.0 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.9 Hz, 1.14H), 0.94 (s, 9H), 0.11 (s, 1.29H), 0.09 (s, 2.85H), 0.09 (s, 1.29H), 0.08 (s, 0.57H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$,

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ppm): δ 146.7 (d, $^4J_{CP}$ = 4.7 Hz), 145.5 (d, $^4J_{CP}$ = 4.7 Hz), 136.7, 136.7, 135.2 (d, $^3J_{CP}$ = 15.9 Hz), 132.9 (d, $^3J_{CP}$ = 15.8 Hz), 131.5, 130.9, 128.53, 128.51, 127.5, 126.44, 126.39, 122.52 (dq, $^1J_{CF}$ = 275.9 Hz, $^3J_{CP}$ = 7.6 Hz), 122.48 (dq, $^1J_{CF}$ = 275.9 Hz, $^3J_{CP}$ = 7.6 Hz), 122.47 (dq, $^1J_{CF}$ = 275.9 Hz, $^3J_{CP}$ = 7.4 Hz), 118.5 (d, $^2J_{CP}$ = 11.4 Hz), 117.0 (d, $^2J_{CP}$ = 13.0 Hz), 115.4 (d, $^5J_{CP}$ = 4.3 Hz), 114.0 (d, $^5J_{CP}$ = 3.0 Hz), 76.40 (d, $^5J_{CP}$ = 2.0 Hz), 74.37 (d, $^5J_{CP}$ = 0.6 Hz), 62.2 (dq, $^2J_{CF}$ = 37.7 Hz, $^2J_{CP}$ = 6.5 Hz), 62.13 (dq, $^2J_{CF}$ = 37.7 Hz, $^2J_{CP}$ = 6.4 Hz), 62.10 (dq, $^2J_{CF}$ = 37.7 Hz, $^2J_{CP}$ = 6.9 Hz), 30.8 (d, $^1J_{CP}$ = 140.5 Hz), 27.1 (d, $^1J_{CP}$ = 142.3 Hz), 25.7, 18.3, −4.8, −4. 9, −4.98, −5.01. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 30.30 (s, minor), 29.35 (s, major). FT-IR (neat, cm^{-1}): 2957, 2931, 2859, 2251, 1720, 1601, 1495, 1472, 1463, 1417, 1362, 1290, 1256, 1171, 1105, 1071, 1006, 963, 908, 880, 835, 777, 732, 693, 649, 602, 556, 520. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{33}F_6O_4PSiNa$ 581.1682, found 581.1690.

*Diethyl (7-((tert-Butyldimethylsilyl)oxy)-5-methylenehept-3-en-1-yl)phosphonate (**3df**).* Compounds **1d** (194 mg, 1.01 mmol), **2f** (47 mg, 0.26 mmol), and **Ru3** (8 mg, 0.13 mmol) were used following general procedure B for 3 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3df** after flash chromatography on silica gel (eluent: 40% to 50% ethyl acetate in hexanes) as a pale-yellow oil with a 1:1.2 *E*/*Z* ratio (67 mg, 70%). Analytical TLC: R_f = 0.20 (50% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 6.04 (d, $^3J_{HH}$ = 15.8 Hz, 0.45H), 5.78 (d, $^3J_{HH}$ = 11.6 Hz, 0.55H), 5.67 (dt, $^3J_{HH}$ = 15.7 Hz, $^3J_{HH}$ = 6.8 Hz, 0.45H), 5.43 (dt, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 7.3 Hz, 0.55H), 5.00 (s, 0.55H), 4.92 (s, 0.45H), 4.87 (s, 0.45H), 4.85 (s, 0.55H), 4.12−3.98 (m, 4H), 3.67 (t, $^3J_{HH}$ = 7.2 Hz, 0.9H), 3.62 (t, $^3J_{HH}$ = 7.1 Hz, 1.1H), 2.52−2.43 (m, 1.1H), 2.41−2.31 (m, 0.9H), 2.38 (t, $^3J_{HH}$ = 7.2 Hz, 0.9H), 2.27 (t, $^3J_{HH}$ = 7.1 Hz, 1.1H), 1.83−1.71 (m, 2H), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 2.7H), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3.3H), 0.84 (s, 4.05H), 0.84 (s, 4.95H), −0.00 (s, 2.7H), −0.00 (s, 3.3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 142.7, 142.0, 132.9 (d, $^5J_{CP}$ = 1.1 Hz), 131.0 (d, $^5J_{CP}$ = 1.8 Hz), 130.6 (d, $^3J_{CP}$ = 17.3 Hz), 128.4 (d, $^3J_{CP}$ = 17.1 Hz), 115.9, 115.6, 62.5, 62.3, 61.59 (d, $^2J_{CP}$ = 6.4 Hz), 61.58 (d, $^2J_{CP}$ = 6.4 Hz), 40.7, 35.8, 26.3 (d, $^1J_{CP}$ = 139.3 Hz), 26.0, 26.0, 25.8 (d, $^2J_{CP}$ = 4.5 Hz), 25.7 (d, $^1J_{CP}$ = 139.1 Hz), 21.9 (d, $^2J_{CP}$ = 4.4 Hz), 18.4, 18.4, 16.6 (d, $^3J_{CP}$ = 7.0 Hz), −5.16, −5.21. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 30.66 (s, minor), 30.65 (s, major). FT-IR (neat, cm^{-1}): 3451, 2954, 2929, 2857, 1636, 1472, 1463, 1443, 1390, 1361, 1248, 1164, 1096, 1055, 1027, 962, 894, 834, 813, 775, 736, 663, 542. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{37}O_4PSiNa$ 399.2091, found 399.2102.

*(±)-Diethyl ((7E)-6-((tert-Butyldimethylsilyl)oxy)-5-methylene-8-phenylocta-3,7-dien-1-yl)phosphonate (**3dh**).* Compounds **1d** (149 mg, 0.77 mmol), **(±)-2h** (68 mg, 0.25 mmol), and **Ru3** (8 mg, 0.13 mmol) were used following general procedure B for 3 h. The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3dh** after flash chromatography on silica gel (eluent: 35% to 40% ethyl acetate in hexanes) as a pale-yellow oil with a 1:1 *E*/*Z* ratio (92 mg, 79%). Analytical TLC: R_f = 0.30 (50% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.37−7.32 (m, 2H), 7.32−7.27 (m, 2H), 7.23−7.18 (m, 1H), 6.58 (d, $^3J_{HH}$ = 15.7 Hz, 0.5H), 6.54 (d, $^3J_{HH}$ = 15.8 Hz, 0.5H), 6.19 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 5.7 Hz, 0.5H), 6.11 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 5.9 Hz, 0.5H), 6.03 (d, $^3J_{HH}$ = 16.0 Hz, 0.5H), 5.94 (dt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.6 Hz, 0.5H), 5.89 (d, $^3J_{HH}$ = 11.7 Hz, 0.5H), 5.58 (dt, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.2 Hz, 0.5H), 5.36 (s, 0.5H), 5.21 (s, 0.5H), 5.08 (s, 0.5H), 4.98 (s, 0.5H), 4.93 (d, $^3J_{HH}$ = 5.5 Hz, 0.5H), 4.71 (d, $^3J_{HH}$ = 5.7 Hz, 0.5H), 4.13−3.98 (m, 4H), 2.56−2.46 (m, 1H), 2.42−2.32 (m, 1H), 1.85−1.70 (m, 2H), 1.30 (t, $^3J_{HH}$ = 6.9 Hz, 1.5H), 1.30 (t, $^3J_{HH}$ = 7.3 Hz, 1.5H), 1.29 (t, $^3J_{HH}$ = 7.0 Hz, 1.5H), 1.28 (t, $^3J_{HH}$ = 7.3 Hz, 1.5H), 0.92 (s, 9H), 0.8 (s, 4H), 0.7 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 147.5, 146.2, 137.1, 137.0, 132.3 (d, $^3J_{CP}$ = 17.8 Hz), 132.1, 132.0, 129.9 (d, $^3J_{CP}$ = 17.5 Hz), 129.6, 129.5, 129.4 (d, $^5J_{CP}$ = 1.4 Hz), 128.61, 128.59, 127.51, 127.49, 127.4 (d, $^5J_{CP}$ = 1.9 Hz), 126.57, 126.57, 113.3, 113.1, 76.7, 74.4, 61.60 (d, $^2J_{CP}$ = 6.5 Hz), 61.57 (d, $^2J_{CP}$ = 6.4 Hz), 26.21 (d, $^2J_{CP}$ = 1.1 Hz), 26.17 (d, $^1J_{CP}$ = 139.1 Hz), 26.0, 25.6 (d, $^1J_{CP}$ = 139.0 Hz), 21.1 (d, $^5J_{CP}$ = 1.1 Hz), 18.49, 18.47, 16.57 (d, $^3J_{CP}$ = 6.0 Hz), 16.55 (d, $^3J_{CP}$ = 6.0 Hz), −4.60, −4.64, −4.7. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 30.80 (s, 0.5P), 30.67 (s, 0.5P). FT-IR (neat, cm^{-1}): 3449, 2955, 2929, 2857, 1601, 1495, 1472, 1463, 1448, 1390, 1361, 1248, 1164, 1099, 1056, 1028, 963, 900, 882, 834, 776, 747, 693, 588, 534. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{41}O_4PSiNa$ 487.2404, found 487.2417.

*(±)-Ethyl 8-((tert-Butyldimethylsilyl)oxy)-2-(diethoxyphosphoryl)-6-methyleneoct-4-enoate (**3ec**).* Compounds **1e** (203 mg, 0.77 mmol), **2c** (40 mg, 0.25 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3ec** after flash chromatography on silica gel (eluent: 20% to 30% acetone in hexanes) as a pale-yellow oil with a 1.5:1 *E*/*Z* ratio (74 mg, 70%). Analytical TLC: R_f = 0.25 (30% acetone in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.06−7.99 (m, 2H), 7.56−7.49 (m, 1H), 7.44−7.38 (m, 2H), 6.18 (d, $^3J_{HH}$ = 16.0 Hz, 0.6H), 5.94 (d, $^3J_{HH}$ = 11.8 Hz, 0.4H), 5.71 (dt, $^3J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 7.1 Hz, 0.6H), 5.52 (dt, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 6.9 Hz, 0.4H), 5.39 (s, 0.4H), 5.25 (s, 0.6H), 5.16 (s, 1.0H), 4.91 (s, 1.2H), 4.81 (s, 0.8H), 4.20−4.05 (m, 6H), 3.07−2.57 (m, 3H), 1.33−1.26 (m, 6H), 1.23 (t, *J* = 7.1 Hz, 1.2H), 1.19 (t, *J* = 7.1 Hz, 1.8H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 168.6 (d, $^2J_{CP}$ = 4.7 Hz), 168.5 (d, $^2J_{CP}$ = 4.7 Hz), 166.2, 166.1, 139.9, 139.5, 133.1 (d, $^5J_{CP}$ = 2.0 Hz), 132.0 (d, $^5J_{CP}$ = 0.5 Hz), 130.10, 130.05, 129.8 (d, $^3J_{CP}$ = 17.0 Hz), 129.7, 129.91, 129.89, 128.43, 128.42, 126.9 (d, $^3J_{CP}$ = 16.1 Hz), 117.3, 117.1, 67.0, 64.4, 62.9 (d, $^2J_{CP}$ = 6.3 Hz), 62.8 (d, $^2J_{CP}$ = 6.8 Hz), 61.52, 61.46, 46.0 (d, $^1J_{CP}$ = 130.3 Hz), 45.6 (d, $^1J_{CP}$ = 129.6 Hz), 30.5 (d, $^2J_{CP}$ = 4.3 Hz), 26.3 (d, $^2J_{CP}$ = 4.2 Hz), 16.41 (d, $^3J_{CP}$ = 6.0 Hz), 16.39 (d, $^3J_{CP}$ = 6.0 Hz), 14.16. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 21.28 (s, major), 21.25 (s, minor). FT-IR (neat, cm^{-1}): 3451, 2982, 2932, 2109, 1721, 1602, 1584, 1451, 1392, 1368, 1315, 1255, 1175, 1153, 1110, 1098, 1022, 967, 860, 792, 713, 688, 674, 651, 559. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{30}O_7P$ 425.1714, found 425.1714.

*Ethyl 8-((tert-butyldimethylsilyl)oxy)-2-(diethoxyphosphoryl)-6-methyleneoct-4-enoate (**3ef**).* Compounds **1e** (266 mg, 1.01 mmol), **2f** (49 mg, 0.26 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3ef** after flash chromatography on silica gel (eluent: 45% ethyl acetate in hexanes) as a pale-yellow oil with a 1.5:1 *E*/*Z* ratio (100 mg, 84%). Analytical TLC: R_f = 0.41 (50% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 6.09 (d, $^3J_{HH}$ = 15.8 Hz, 0.6H), 5.85 (d, $^3J_{HH}$ = 11.7 Hz, 0.4H), 5.59 (dt, $^3J_{HH}$ = 15.7 Hz, $^3J_{HH}$ = 7.1 Hz, 0.6H), 5.37 (dt, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 7.1 Hz, 0.4H), 5.05−5.02 (m, 0.4H), 4.95−4.93 (m, 0.6H), 4.92−4.88 (m, 1H), 4.22−4.07 (m, 6H), 3.66 (t, $^3J_{HH}$ = 7.3 Hz, 1.2H), 3.64 (t, $^3J_{HH}$ = 7.2 Hz, 0.8H), 2.98 (ddd, $^2J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 4.0 Hz, 0.6H), 2.94 (ddd, $^2J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 4.0 Hz, 0.6H), 2.89−2.81 (m, 0.4H), 2.81−2.67 (m, 1H), 2.65−2.56 (m, 0.6H), 2.36 (t, $^3J_{HH}$ = 7.3 Hz, 1.2H), 2.29 (t, $^3J_{HH}$ = 7.1 Hz, 1.8H), 0.86 (s, 9H), 0.02 (s, 2.4H), 0.01 (s, 3.6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 168.8 (d, $^2J_{CP}$ = 4.7 Hz), 168.6 (d, $^2J_{CP}$ = 4.3 Hz), 142.4, 141.8, 134.8 (d, $^5J_{CP}$ = 0.8 Hz), 132.5 (d, $^5J_{CP}$ = 1.4 Hz), 127.6 (d, $^3J_{CP}$ = 15.9 Hz), 125.4 (d, $^3J_{CP}$ = 16.1 Hz), 116.5, 115.9, 62.92 (d, $^2J_{CP}$ = 6.4 Hz), 62.89 (d, $^2J_{CP}$ = 6.2 Hz), 62.8 (d, $^2J_{CP}$ = 6.9 Hz), 62.7 (d, $^2J_{CP}$ = 7.1 Hz), 62.35, 62.33, 61.49, 61.46, 46.2 (d, $^1J_{CP}$ = 130.3 Hz), 45.9 (d, $^1J_{CP}$ = 129.4 Hz), 40.6, 35.7, 30.4 (d, $^2J_{CP}$ = 4.3 Hz), 26.2 (d, $^2J_{CP}$ = 4.3 Hz), 26.0, 18.40, 18.37, 16.46 (d, $^2J_{CP}$ = 6.0 Hz), 16.44 (d, $^2J_{CP}$ = 6.2 Hz), 14.25, 14.23, −5.20, −5.23. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ 21.42 (s, minor), 21.37 (s, major). FT-IR (neat, cm^{-1}): 2955, 2930, 2857, 1734, 1607, 1472, 1444, 1390, 1368, 1327, 1252, 1152, 1096, 1023, 967, 894, 834, 812, 775, 732, 663, 602, 566. High-resolution MS HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{41}O_6PSiNa$ 471.2302, found 471.2314.

*6-((tert-Butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl diethyl Phosphate (**3ff**).* Compounds **1f** (198 mg, 1.02 mmol), **2f** (48 mg, 0.26 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with

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methanolic potassium isocyanoacetate, which afforded **3ff** after flash chromatography on silica gel (eluent: 40% ethyl acetate in hexanes) as a pale-yellow oil with a 2:1 *E*/*Z* ratio (75 mg, 77%). Analytical TLC: R_f = 0.30 (30% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.30 (ddt, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 1.5 Hz, $^4J_{HH}$ = 0.5 Hz, 0.65H), 6.02 (ddt, $^3J_{HH}$ = 11.7 Hz, $^3J_{HP}$ = 1.9 Hz, $^4J_{HH}$ = 1.0 Hz, 0.35H), 5.79 (dt, $^3J_{HH}$ = 15.8 Hz, $^3J_{HP}$ = 6.3 Hz, 0.65H), 5.67 (dt, $^3J_{HH}$ = 11.7 Hz, $^3J_{HP}$ = 6.4 Hz, 0.35H), 5.09−5.07 (m, 1H), 5.05 (s, 0.65H), 4.80−4.77 (m, 0.35H), 4.71 (ddd, $^2J_{HP}$ = 8.1 Hz, $^3J_{HH}$ = 6.5 Hz, $^2J_{HH}$ = 1.7 Hz, 0.7H), 4.57 (ddd, $^2J_{HP}$ = 8.1 Hz, $^3J_{HH}$ = 6.4 Hz, $^2J_{HH}$ = 1.2 Hz, 1.3H), 4.13−4.05 (m, 4H), 3.71 (t, $^3J_{HH}$ = 7.1 Hz, 1.3H), 3.64 (t, $^3J_{HH}$ = 6.9 Hz, 0.7H), 2.42 (dt, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 0.9 Hz, 1.3H), 2.29 (dt, $^3J_{HH}$ = 6.9 Hz, $^2J_{HH}$ = 0.9 Hz, 0.7H), 1.33−1.29 (m, 6H), 0.86 (s, 5.85H), 0.86 (s, 3.15H), 0.02 (s, 3.3H), 0.02 (s, 2.7H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 142.0, 141.6, 136.2, 134.0, 126.6 (d, *J* = 7.3 Hz), 123.1 (d, *J* = 6.8 Hz), 118.7, 117.0, 68.0, 67.9, 63.9 (d, $^2J_{CP}$ = 5.7 Hz), 63.8 (d, $^2J_{CP}$ = 5.1 Hz), 62.2, 62. 40.2, 35.6, 26.00, 25.98, 18.4, 18.3, 16.2 (d, $^2J_{CP}$ = 6.7 Hz), −5.2, −5.3. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ −1.28 (s, major), −1.30 (s, minor). FT-IR (neat, cm^{-1}): 2954, 2930, 2857, 1608, 1583, 1473, 1444, 1418, 1392, 1370, 1257, 1192, 1167, 1097, 1027, 969, 900, 833, 775, 732, 663, 631, 518. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{35}O_6PSiNa$ 401.1884, found 401.1881.

*(6E)-5-((tert-Butyldimethylsilyl)oxy)-4-methylene-7-phenylhepta-2,6-dien-1-yl Diethyl Phosphate (**3fh**).* **1f** (152 mg, 0.78 mmol), (±)-**2h** (71 mg, 0.26 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3fh** after flash chromatography on silica gel (eluent: 25% to 30% ethyl acetate to hexanes) as a pale-yellow oil with a 2:1 *E*/*Z* ratio (77.8 mg, 64%). Analytical TLC: R_f = 0.16 (30% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.37−7.33 (m, 2H), 7.31−7.26 (m, 2H), 7.23−7.18 (m, 1H), 6.59 (d, $^3J_{HH}$ = 15.9 Hz, 0.6H), 6.56 (d, $^3J_{HH}$ = 15.8 Hz, 0.4H), 6.27 (d, $^3J_{HH}$ = 16.0 Hz, 0.6H), 6.18 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 5.6 Hz, 0.6H), 6.13 (d, $^3J_{HH}$ = 11.9 Hz, 0.4H), 6.10 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 5.9 Hz, 0.4H), 6.03 (dt, $^3J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 6.2 Hz, 0.6H), 5.79 (dt, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 6.4 Hz, 0.4H), 5.40 (s, 0.4H), 5.36 (s, 0.6H), 5.21 (s, 0.6H), 4.96 (d, $^3J_{HH}$ = 5.8 Hz, 0.6H), 4.88 (s, 0.4H), 4.76−4.69 (m, 1.2H), 4.58−4.53 (m, 1.2H), 4.11−3.99 (m, 4H), 1.31−1.24 (m, 6H), 0.92 (s, 9H), 0.09 (s, 2H), 0.08 (s, 2H), 0.07 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 146.7, 145.8, 136.92, 136.85, 132.4, 131.6, 131.1, 130.5 (d, $^4J_{CP}$ = 0.9 Hz), 130.0, 129.8, 128.59, 128.57, 128.1 (d, $^3J_{CP}$ = 7.6 Hz), 127.61, 127.57, 126.59, 126.56, 124.7 (d, $^3J_{CP}$ = 6.6 Hz), 115.8, 114.8, 76.3, 74.3, 68.11, 68.07, 68.09 (d, $^2J_{CP}$ = 5.5 Hz), 64.4 (d, $^2J_{CP}$ = 5.3 Hz), 63.8 (d, $^2J_{CP}$ = 5.8 Hz), 25.90, 25.89, 18.4, 16.2 (d, $^3J_{CP}$ = 6.7 Hz), 16.1 (d, $^2J_{CP}$ = 6.6 Hz), −4.6, −4.7, −4.8. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ −1.39 (s, major), −1.42 (s, minor). FT-IR (neat, cm^{-1}): 2955, 2930, 2857, 2112, 1601, 1495, 1472, 1463, 1449, 1391, 1369, 1258, 1166, 1101, 1026, 967, 902, 881, 834, 776, 747, 693, 597, 528. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{39}O_5PSiNa$ 489.2186, found 489.2191.

*O,O-Diethyl (5-Hydroxy-4-methylenehex-2-en-1-yl)-phosphonothioate (**3gb**).* Compounds **1g** (147 mg, 0.75 mmol), **2b** (43 mg, 0.25 mmol), and **Ru3** (8 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3gb** after flash chromatography on silica gel (eluent: 5% ethyl acetate in hexanes) as a mixture with the homodimer of **1g** as a clear colorless oil upon isolation. Analytical TLC: R_f = 0.17 (5% ethyl acetate in hexanes).

The isolated mixture was added to a 25 mL rb flask and subsequently dissolved in anhydrous methanol (5 mL, ca. 0.05M). K_2CO_3 (53 mg, 0.38 mmol) was then added and the reaction mixture was allowed to stir overnight (ca. 18 h). The reaction mixture was then diluted with EtOAc (5 mL) and subsequently extracted with a saturated aqueous solution of NH_4Cl (5 mL). The organic layer was removed and the aqueous layer was extracted with additional EtOAc (3x, 10 mL). The organic layers were combined and were then extracted with a saturated aqueous solution of K_2CO_3 (10 mL) and brine (10 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated via rotatory evaporation and purified by flash column chromatography on silica gel (eluent: 15% to 20% ethyl acetate in hexanes) to afford **3gb** as a clear colorless oil with a 2:1 *E*/*Z* ratio (50 mg, 75% over two steps). Analytical TLC: R_f = 0.19 (20% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.18−6.11 (m, 0.35H), 6.13 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 6.0 Hz, 0.65H), 5.75 (ddt, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.65H), 5.69 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 7.8 Hz, 0.35H), 5.24 (s, 0.35H), 5.21 (s, 0.65H), 5.09 (s, 0.35H), 5.05 (s, 0.65H), 4.56 (q, $^3J_{HH}$ = 6.3 Hz, 0.65H), 4.28 (q, $^3J_{HH}$ = 6.5 Hz, 0.35H), 4.19−3.99 (m, 35H), 3.09−2.93 (m, 0.7H), 2.82 (dd, $^2J_{HP}$ = 19.8 Hz, $^3J_{HH}$ = 7.6 Hz, 1.3H), 1.95 (bs, 0.35H), 1.79 (bs, 0.66H), 1.34 (d, $^3J_{HH}$ = 6.4 Hz, 1.95H), 1.30−1.24 (m, 7.05H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 149.7 (d, $^4J_{CP}$ = 4.8 Hz), 148.2 (d, $^4J_{CP}$ = 3.8 Hz), 134.5 (d, $^3J_{CP}$ = 15.8 Hz), 131.2 (d, $^3J_{CP}$ = 15.6 Hz), 122.4 (d, $^2J_{CP}$ = 9.6 Hz), 119.5 (d, $^2J_{CP}$ = 11.3 Hz), 112.9, 112.9, 70.8 (d, $^5J_{CP}$ = 1.9 Hz), 67.7, 62.9 (d, $^2J_{CP}$ = 7.1 Hz), 62.83 (d, $^2J_{CP}$ = 6.8 Hz), 62.82 (d, $^2J_{CP}$ = 7.1 Hz), 62.77 (d, $^2J_{CP}$ = 6.8 Hz), 40.0 (d, $^1J_{CP}$ = 109.8 Hz), 35.6 (d, $^1J_{CP}$ = 111.1 Hz), 22.9, 22.3, 16.29 (d, $^3J_{CP}$ = 6.7 Hz), 16.26 (d, $^3J_{CP}$ = 7.0 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 93.48 (s, minor), 92.81 (s, major). FT-IR (neat, cm^{-1}): 3412, 2979, 1444, 1389, 1160, 1099, 1024, 957, 869, 841, 780, 598. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{11}H_{21}O_3PSNa$ 287.0841, found 287.0841.

*O,O-Diethyl (6-Hydroxy-4-methylenehex-2-en-1-yl)-phosphonothioate (**3gf**).* Compounds **1g** (151 mg, 0.78 mmol), **2f** (47 mg, 0.26 mmol), and **Ru3** (8.0 mg, 0.013 mmol) were used following general procedure A (ca. 0.05 M). The catalyst was quenched with methanolic potassium isocyanoacetate, which afforded **3gf** after flash chromatography on silica gel (eluent: 2% to 3% ethyl acetate in hexanes) as a mixture with **1g** as a clear colorless oil upon isolation. Analytical TLC: R_f = 0.45 (5% ethyl acetate in hexanes).

The isolated mixture was added to a 25 mL of rb flask and subsequently dissolved in anhydrous ethanol (5 mL). Pyridinium *p*-toluenesulfonate (26 mg, 0.10 mmol) was then added, and the reaction mixture was allowed to stir overnight (ca. 18 h). The reaction mixture was then concentrated and purified by flash column chromatography on silica gel (eluent: 20% to 25% ethyl acetate in hexanes) to afford **3gf** as a clear colorless oil with a 5:1 *E*/*Z* ratio (41 mg, 61% over two steps). Analytical TLC: R_f = 0.23 (20% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.17 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 5.8 Hz, 0.83H), 6.04 (dd, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 11.5 Hz, 0.17H), 5.68 (ddt, $^3J_{HH}$ = 15.7 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 0.83H), 5.60 (ddt, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HP}$ = 7.9 Hz, 0.17H), 5.10 (s, 0.34H), 5.07 (s, 0.83H), 5.02 (s, 0.83H), 4.16−4.00 (m, 4H), 3.73 (t, $^3J_{HH}$ = 6.4 Hz, 1.66H), 3.68 (t, $^3J_{HH}$ = 6.2 Hz, 0.34H), 3.04 (dd, $^2J_{HP}$ = 20.0 Hz, $^3J_{HH}$ = 7.9 Hz, 0.34H), 2.83 (dd, $^2J_{HP}$ = 19.9 Hz, $^3J_{HH}$ = 7.6 Hz, 1.66H), 2.49 (t, $^3J_{HH}$ = 6.4 Hz, 1.66H), 2.35 (t, $^3J_{HH}$ = 6.1 Hz, 0.34H), 1.28 (t, $^3J_{HH}$ = 7.0 Hz, 1.02H), 1.27 (t, $^3J_{HH}$ = 7.0 Hz, 4.98H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 142.2 (d, $^4J_{CP}$ = 4.9 Hz), 141.5 (d, $^4J_{CP}$ = 3.7 Hz), 136.7 (d, $^3J_{CP}$ = 15.5 Hz), 134.2 (d, $^3J_{CP}$ = 15.8 Hz), 120.9 (d, $^2J_{CP}$ = 9.3 Hz), 119.3 (d, $^2J_{CP}$ = 11.2 Hz), 117.4 (d, $^5J_{CP}$ = 4.5 Hz), 116.7 (d, $^5J_{CP}$ = 2.7 Hz), 62.9 (d, $^2J_{CP}$ = 7.0 Hz), 61.2, 60.7, 40.4 (d, $^5J_{CP}$ = 2.0 Hz), 39.7 (d, $^1J_{CP}$ = 110.0 Hz), 35.6, 35.5 (d, $^1J_{CP}$ = 111.1 Hz), 16.31 (d, $^3J_{CP}$ = 6.7 Hz), 16.28 (d, $^3J_{CP}$ = 6.8 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): δ 93.60 (s, minor), 92.83 (s, major). FT-IR (neat, cm^{-1}): 3401, 2980, 2934, 2901, 2115, 1606, 1443, 1389, 1293, 1217, 1160, 1097, 1019, 954, 893, 864, 825, 763, 600. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{11}H_{21}O_3PSNa$ 287.0841, found 287.0841.

*(4E/Z,6E)-3-Methylene-7-phenylhepta-4,6-dien-2-yl benzoate (**4ab**).* Compounds **3ab** (2:1 *E*/*Z*, 124 mg, 0.35 mmol) was added to a 25 mL rb flask and was dissolved in THF (3 mL). The flask was then cooled to −78 °C and a solution of KHMDS (66 mg, 0.33 mmol) in THF (1.5 mL), which was prepared in a glovebox, was slowly added and allowed to stir for 1 h at −78 °C. Benzaldehyde (32 mg, 0.30 mmol) was dissolved in THF (1.5 mL) and then slowly

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added to the ylide of **3ab**. The reaction mixture was then allowed to stir and warm to room temperature overnight. A saturated aqueous solution of NH_4Cl (5 mL) was added and the organic layer was removed. The aqueous layer was then extracted with Et_2O (2x, 15 mL). The organic layers were then combined and extracted with water (10 mL) and brine (10 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated via rotatory evaporation and the crude residue was purified by flash column chromatography on silica gel (eluent: 0% to 2% ethyl acetate in hexanes) to afford **4ab** as a clear yellow oil with a 2:1 *EE*:*ZE* ratio (43 mg, 47%). Only the *E*-isomer was observed from olefination, whereas the *E*/*Z* isomer from metathesis was retained. Analytical TLC: R_f = 0.19 (1% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.11−8.07 (m, 1H), 8.05−8.01 (m, 0.65H), 7.59−7.52 (m, 1H), 7.49−7.38 (m, 3.35H), 7.36−7.28 (m, 2.65H), 7.25−7.20 (m, 1H), 7.01 (dd, $^3J_{HH}$ = 15.8, 11.2 Hz, 0.35H), 6.83 (dd, $^3J_{HH}$ = 15.5, 10.4 Hz, 0.65H), 6.62 (d, $^3J_{HH}$ = 15.5 Hz, 0.65H), 6.61 (dd, $^3J_{HH}$ = 15.6, 10.1 Hz, 0.65H), 6.49 (d, $^3J_{HH}$ = 11.4 Hz, 0.35H), 6.39 (d, $^3J_{HH}$ = 15.9 Hz, 0.65H), 6.37 (d, $^3J_{HH}$ = 15.9 Hz, 0.35H), 6.28 (dd, $^3J_{HH}$ = 11.4, 11.4 Hz, 0.35H), 5.89 (q, $^3J_{HH}$ = 6.5 Hz, 0.65H), 5.80 (q, $^3J_{HH}$ = 6.6 Hz, 0.35), 5.36 (s, 0.65H), 5.36 (s, 0.35H), 5.25 (s, 0.65H), 5.25 (s, 0.35H), 1.58 (d, $^3J_{HH}$ = 6.6 Hz, 1.95H), 1.55 (d, $^3J_{HH}$ = 6.5 Hz, 1.05H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 165.9, 165.8, 146.5, 146.4, 137.5, 137.4, 133.8, 133.5, 133.11, 133.06, 131.8, 131.0, 130.6, 130.4, 130.1, 129.79, 129.77, 129.75, 129.3, 129.0, 128.8, 128.53, 128.50, 128.47, 127.8, 127.3, 126.6, 126.3, 115.8, 114.9, 70.9, 70.5, 20.8, 20.5. FT-IR (neat, cm^{-1}): 3025, 2983, 2932, 1715, 1601, 1584, 1491, 1450, 1373, 1314, 1271, 1176, 1107, 1081, 1069, 1026, 987, 948, 900, 805, 777, 749, 711, 690, 618, 505. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{21}H_{20}O_2Na$ 327.1355, found 327.1343.

*(±)-Ethyl (E/Z)-2-((7-(2-((tert-Butyldimethylsilyl)oxy)ethyl)-1,3-dioxo-2-phenyl-2,3,5,8-tetrahydro-1H-[1,2,4]triazolo[1,2-a]-pyridazin-5-yl)methyl)-3-phenylacrylate (**4ef**).* Compound **3ef** (107 mg, 0.24 mmol) was added to a 25 mL rb flask and was subsequently dissolved in CH_2Cl_2 (ca. 0.05 M). 4-Phenyl-1,2,4-triazole-3,5-dione (41 mg, 0.24 mmol) was freshly prepared following the literature procedure[51] and was added to the rb flask, which formed a dark red solution. The reaction mixture was then allowed to stir for 2 h, which afforded a light pink solution. TLC analysis showed consumption of the diene.

The reaction mixture was then concentrated and dissolved in THF (5 mL). NaH (60% dispersion in mineral oil; 10 mg, 0.26 mmol) was then added and the mixture was allowed to stir for one hour; This afforded a yellow solution upon formation of the ylide. Benzaldehyde (27 mg, 0.26 mmol) was dissolved in THF (1.5 mL) and was slowly added to the ylide. The reaction mixture was then allowed to stir overnight, which afforded a pale orange solution. A saturated aqueous solution of NH_4Cl (5 mL) was added and the organic layer was removed. The aqueous layer was then extracted with Et_2O (2×, 10 mL). The organic layers were then combined and extracted with water (10 mL) and brine (10 mL). The organic layer was then dried with $MgSO_4$, which was subsequently removed via gravity filtration through filter paper. The dried organic layer was then concentrated via rotatory evaporation and the crude residue was purified by flash column chromatography on silica gel to afford **4ef** after flash chromatography on silica gel (eluent: 15% to 20% ethyl acetate in hexanes) as a clear light orange oil with a 3:1 *E*/*Z* ratio (102 mg, 75% over two steps). Analytical TLC: R_f = 0.55 (25% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.79 (s, 0.75H), 7.51−7.17 (m, 10H), 6.77 (s, 0.25H), 5.77−5.72 (m, 0.25H), 5.59−5.55 (m, 0.75H), 4.90−4.81 (m, 1H), 4.26 (q, $^3J_{HH}$ = 7.1 Hz, 1.5H), 4.24 (d, $^3J_{HH}$ = 16.0 Hz, 0.25H), 4.19 (d, $^3J_{HH}$ = 16.4 Hz, 0.75H), 4.11−4.03 (m, 0.5H), 3.99 (dt, $^3J_{HH}$ = 16.2 Hz, $^4J_{HH}$ = 2.2 Hz, 0.25H), 3.90 (dt, $^3J_{HH}$ = 16.3 Hz, $^4J_{HH}$ = 2.2 Hz, 0.75H), 3.73 (t, $^3J_{HH}$ = 6.4 Hz, 0.5H), 3.65 (t, $^3J_{HH}$ = 6.4 Hz, 1.5H), 3.23 (dd, $^2J_{HH}$ = 13.9 Hz, $^5J_{HH}$ = 6.6 Hz, 0.75H), 3.00 (dd, $^2J_{HH}$ = 13.7 Hz, $^5J_{HH}$ = 6.5 Hz, 0.75H), 2.98−2.91 (m, 0.5H), 2.39−2.27 (m, 0.5H), 2.24 (t, $^3J_{HH}$ = 6.3 Hz, 1.5H), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 2.25H), 1.06 (t, $^3J_{HH}$ = 7.1 Hz, 0.75H), 0.89 (s, 2.25H), 0.88 (s, 6.75H), 0.05 (s, 1.5H), 0.04 (s, 2.25H), 0.03 (s, 2.25H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 168.5, 167.9, 153.5, 152.9, 151.2, 150.8, 141.9, 139.1, 135.9, 135.3, 131.50, 131.49, 131.4, 131.1, 129.2, 129.1, 129.0, 128.83, 128.75, 128.5, 128.3, 128.1, 128.04, 128.02, 127.9, 125.6, 125.4, 120.9, 120.6, 62.0, 61.8, 61.2, 60.8, 52.8, 52.0, 47.0, 46.5, 38.6, 37.8, 37.7, 30.5, 29.7, 25.9, 18.28, 18.26, 14.4, 13.8, −5.3. FT-IR (neat, cm^{-1}): 2954, 2929, 2856, 2252, 1773, 1709, 1631, 1601, 1503, 1471, 1458, 1412, 1291, 1252, 1219, 1201, 1174, 1134, 1096, 1027, 1006, 974, 911, 835, 811, 775, 766, 731, 689, 663, 645, 617, 547, 506. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{32}H_{42}N_3O_5Si$ 576.2888, found 576.2902.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02886.

NMR spectra for new compounds (PDF)

FAIR data, including the primary NMR FID files, for compounds **1g**, **2h**, **3aa**−**al**, **3bf**, **3bj**, **3cb**, **3cd**, **3ch**, **3df**, **3dh**, **3ec**, **3ef**, **3ff**, **3fh**, **3gb**, **3gf**, **4ab**, and **4ef** (ZIP)

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Notes

The authors declare no competing financial interest.

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